Pergamon

Tetrahedron Letters 39 (1998) 2869–2872

TETRAHEDRON
LETTERS

Aerobic Epoxidation of Olefins Catalysed by Square-Planar Nickel(II) Complexes of Bis-*N,N'*-disubstituted Oxamides and Related Ligands

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Received 31 December 1997; revised 2 February 1998; accepted 6 February 1998

Abstract: The new square-planar nickel(II) complexes of *o*-phenylenebis(*N'*-methyloxamidate) and related ligands catalyse the aerobic epoxidation of olefins with co-oxidation of pivalaldehyde; the modulation of catalytic activity by substituents along this series of metal complexes points out the role of high-valent nickel(IV)-oxo species as the putative intermediate in these oxygen atom transfer reactions.
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The use of transition-metal complexes as catalysts for epoxidation reactions has received increase attention during the last decades, particularly by the interest in understanding reactions of biological importance where the metal ion plays a central role.[1] However, despite the extensive studies carried out with cobalt, iron and manganese complexes,[2-4] only a few investigations have focused on nickel catalysts.[5-8] The best studied example is the nickel(II) cyclam complex, cyclam being the tetraamine macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane, which can achieve the catalytic epoxidation of olefins using iodosylbenzene[5,6] or *m*-chloroperbenzoic acid[7a] as oxidants. The catalytic activity has been tentatively ascribed to an oxo-nickel(IV) reactive intermediate. However, the formal potential for the Ni(III)/Ni(II) couple of $[Ni(cyclam)]^{2+}$ is moderately positive, *i.e.* 0.97 V *vs.* SCE (CH_3CN, 25 °C, 0.1 mol dm^{-3} NEt_4BF_4) and, moreover, the Ni(IV)/Ni(III) conversion is not avalaible for this system under these conditions.[9] In fact, no well-characterized high-valent terminal metal-oxo species are found to the right of iron in the periodic table, oxo groups being readily found in bridging environments in that case.[10] Here we present indirect but convincing evidence for the possible existence of such species.

Our approach makes use of polychelating tetraamido-*N* ligands like *o*-phenylenebis(*N'*-methyloxamidate) (Me_2opba), its oxamate (Meopba) and bis(oxamate) (opba) derivatives, which have large donor capacities due to the presence of the deprotonated amido groups such that unusually high and otherwise unstable oxidation state complexes of later first row transition metals ions can be attained.[4,11] In this regard, the diamagnetic low-spin four-coordinated square-planar nickel(II)-Me_2opba complex experiences not only one but two one-electron oxidations at 0.13 and 0.90 V *vs.* SCE (CH_3CN, 25 °C, 0.1 mol dm^{-3} NEt_4ClO_4). The first oxidation is reversible and readily corresponds to the Ni(II)-Ni(III) redox process. The second oxidation is pseudo-reversible and can be tentatively assigned to the Ni(III)-Ni(IV) oxidation process, even if a ligand-centered oxidation of the aromatic ring leading to a Ni(III)-ligand radical species cannot be definitively discarded.

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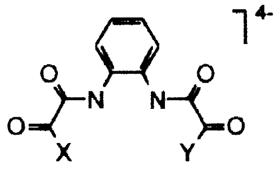
PII: S0040-4039(98)00321-9



X	Y	Ligand
N(CH$_3$)	N(CH$_3$)	Me$_2$opba
N(CH$_3$)	O	Meopba
O	O	opba

With the establishment that this nickel complex is capable of readily undergoing two-electron changes, such as is commonly thought for the more conventional catalytic systems based on iron or manganese complexes,[1] the question arises whether this system is effective in catalysis. The results obtained for the epoxidation of some representative tri- and disubstituted olefins, both cyclic and acyclic, using dioxygen as oxidant in the presence of pivalaldehyde as reducing agent are detailed in Table 1. Indeed, the nickel(II)-Me$_2$opba complex can be considered as an effective catalyst, even if its catalytic efficiency is somewhat reduced compared to that of the related nickel(II)-Meopba and nickel(II)-opba complexes, as exemplified by the epoxidation of *trans*-stilbene (entries 1-3). Furthermore, the catalytic epoxidation is greatly stereodependent as indicated by the different yields obtained with *trans*- and *cis*-stilbene (entries 3 and 4, respectively). By contrast, for the epoxidation of olefins by iodosylbenzene in the presence of the nickel(II)-cyclam complex only small amounts of epoxides were produced and, more importantly, in a non-stereodependent manner, *v.g.*, 36 and 38 % yield for *trans*- and *cis*-β-methylstyrene, respectively.[5] Interestingly, no epoxides at all were produced with the nickel(II)-cyclam complex under the same set of conditions used herein.[7b]

Recent studies by Valentine *et al.*[7b] demonstrate that the metal complex plays different roles in the epoxidation of olefins by molecular oxygen with co-oxidation of aldehydes, as illustrated in Scheme 1. It aids in the initiation step for the free radical autooxidation of the aldehyde (eq. 1). The acylperoxy radicals generated in the autooxidation reaction react with olefins to yield epoxides either directly or *via* a metal-acylperoxo complex (eqs. 2 and 3). However, this metal-acylperoxo species could eventually lead to a metal-oxo species by homolytic O-O cleavage of the acylperoxo group (eq. 4). Hydrogen atom abstraction from aldehyde renders the corresponding acid as one of the final products, regenerating thus the initial free radical which starts a new catalytic cycle (eq. 5). Following this simplified scheme, the active intermediate in our catalytic system would be a nickel(IV)-oxo species formed by a two-electron oxidation of the nickel(II) by dioxygen plus pivalaldehyde (the presence of traces of peroxidic radical impurities in the aldehyde sample would account for the initiation step in that case). Epoxidation of olefins should then result from the homolytic addition of the oxo-metal species to the double bond followed by homolytic cyclization (eqs. 6 and 7). This view is supported by the observation that for *cis*-stilbene the reaction product was *trans*-stilbene oxide (entry 4), in agreement with the free rotation of the C-C bond in the postulated transition state for an asynchron C-O bond formation. That being so, nickel(II) complexes with high potentials for the redox couples Ni(III)/Ni(II) and Ni(IV)/Ni(III) should be more efficient in the epoxidation reaction, *i.e.*, the corresponding nickel(IV) species is a stronger oxidant.[1] As mentioned above, decreasing the number of amido donor groups, such as for the Meopba and opba ligands, enhances the catalytic activity of the corresponding nickel(II) complex in measure with the electron defficient character at the metal center as evaluated by the increasing redox potentials. For instance, the Ni(III)/Ni(II) and Ni(IV)/Ni(III) formal potential values for [Ni(opba)]$^{2-}$ are increased by 370 mV (0.50 V *vs.* SCE) and 100 mV (1.00 V *vs.* SCE), respectively, compared to those of [Ni(Me$_2$opba)]$^{2-}$. Thus, the trend in the final yields of epoxides along this series can be rationalized assuming the participation of high-valent (nickel(IV)-oxo) metal intermediates as the active epoxidizing agent.

Table 1. Epoxidation of Olefins by Dioxygen and Pivalaldehyde Catalysed by Nickel(II) Complexes of Bis-*N,N'*-disubstituted Oxamides and Related Ligands[a,b]

Entry	Ligand	Substrate	Time/h	Yield(%)[c,d]
1	opba	*trans*-stilbene	1.5	95
2	Meopba	*trans*-stilbene	1.5	84[e]
3	Me_2opba	*trans*-stilbene	1.5	76[f]
4	Me_2opba	*cis*-stilbene	4.0	28[g,h]
5	Me_2opba	*trans*-β-methylstyrene	1.5	78
6	Me_2opba	1,2-dihydronaphthalene	1.5	82
7	Me_2opba	indene	2.0	84
8	Me_2opba	β-citronellol	2.5	90
9	Me_2opba	β-citronellol methylether	4.5	95
10	Me_2opba	β-citronellol acetate	2.5	90
11	Me_2opba	β-citronellol *tert*-butyl-dimethylsilylether	2.5	92

[a] Reactions were carried out as in ref. 4. [b] The reactions carried out under these conditions were partially heterogeneous. In fact, the orange-yellow nickel(II) tetramethylammonium salt **1** is almost insoluble in fluorobenzene (the nickel content in the solution is undetectable by absorption spectrophotometry), and it is unreactive towards dioxygen even after large periods of oxygenation over O_2 pressure. Addition of pivalaldehyde to the reaction mixture produces an instantaneous change of color of the suspended solid from orange-yelow to green. This is also accompanied by the development of a pale-green color from the solution. We have verified that the filtered solution after treatment with dioxygen plus pivalaldehyde is able to epoxidise alkene substrates, even if somewhat lower yields of epoxide were obtained in this homogeneous system (the nickel concentration as determined by absorption spectrophotometric measurements was 0.1 mmol dm^{-3}). The dark-green solid which was isolated and identified as the (μ-oxo)nickel(III) dimer would be formed by the association of the readily generated oxo-nickel(IV) with the initial nickel(II) complex as described by Kochi (ref. 5). Notwhistanding, its reduced ability to epoxidise olefins precludes it as the viable intermediate responsible for epoxidation and, consequently, supports a nickel(IV)-oxo species as the more probable candidate to play the role of the active epoxidizing agent (see text). [c] Yields refer to isolated and pure epoxidation products. [d] In the absence of catalyst some extension of epoxidation was observed. [e] The final conversion was 95% after 2.0 h. [f] The final conversion was 95% after 2.5 h. [g] With a reaction time of 24 h the final conversion was identical. [h] The reaction product was *trans*-stilbene oxide.

Scheme 1. Mechanism for the Metal-Catalysed Aerobic Epoxidation of Olefins with Co-Oxidation of Aldehyde to Carboxylic Acid

$$RCHO + LM^{III} \rightarrow RCO\bullet + LM^{II} + H^+ \tag{1}$$

$$RCO\bullet + O_2 \rightarrow RCO\text{-}OO\bullet \tag{2}$$

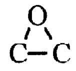
$$RCO\text{-}OO\bullet + LM^{II} \rightarrow RCO\text{-}OO\text{-}M^{III}L \tag{3}$$

$$RCO\text{-}OO\text{-}M^{III}L \rightarrow O{=}M^{IV}L + RCOO\bullet \tag{4}$$

$$RCOO\bullet + RCHO \rightarrow RCOOH + RCO\bullet \tag{5}$$

$$C{=}C + O{=}M^{IV}L \rightarrow \bullet C\text{-}C\text{-}O\text{-}M^{III}L \tag{6}$$

$$\bullet C\text{-}C\text{-}O\text{-}M^{III}L \rightarrow M^{II}L + \tag{7}$$



Synthesis and selected data for the nickel(II) complexes: The tetramethylammonium salts of the nickel(II) complexes were prepared by following a procedure analogous to that described previously for the corresponding copper(II) salts:[11] to a suspension of the free ligand (5 mmol) in methanol (100 cm^3) was added a 25% methanol solution (10 cm^3) of NMe_4OH (25 mmol). A methanolic solution (50 cm^3) of $Ni(ClO_4)_2 \cdot 6H_2O$ (5 mmol) was then added dropwise under stirring. The orange solution was filtered to eliminate the solid NMe_4ClO_4, reduced to *ca.* 10 cm^3 on a rotatory evaporator, and treated sucessively with ether and acetone to give a hygroscopic orange-yellow solid which was rapidly filtered off and dried under vacuum (75-80%). Satisfactory elemental analyses (C, H, N, Ni) were obtained for $[NMe_4]_2[Ni(Me_2opba)] \cdot 4H_2O$ **1**, $[NMe_4]_2[Ni(Meopba)] \cdot 5H_2O$ **2** and $[NMe_4]_2[Ni(opba)] \cdot 6H_2O$ **3**. $\delta_H[(CD_3)_2SO]$ 2.38 (6 H, s, 2 NCH_3), 6.43 (2 H, dd, *m*-H of C_6H_4) and 7.94 (2 H, dd, *o*-H of C_6H_4) for **1**; 2.37 (3 H, s, NCH_3), 6.48 (2 H, dd, *m*-H of C_6H_4) and 7.80 (2 H, dd, *o*-H of C_6H_4) for **2**; 6.53 (2 H, dd, *m*-H of C_6H_4) and 7.78 (2 H, dd, *o*-H of C_6H_4) for **3**. $\nu_{max}(CO)/cm^{-1}$ (KBr) 1590s and 1608vs for **1**; 1612vs (br) and 1660s (sh) for **2**; 1635vs and 1663s (sh) for **3**. λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) ($CH_3CN$) 410 (sh), 357 (6200) and 256 (21900) for **1**; 410 (sh), 380 (sh), 350 (5400), 280 (sh) and 253 (23100) for **2**; 465 (sh), 350 (7200), 275 (sh) and 250 (23100) for **3**.

Acknowledgements. This work was supported by the DGICYT, Ministerio de Educación y Ciencia (Spain) through project PB94-0985. R. Ruiz thanks the Ministerio de Educación y Ciencia (Spain) for a grant.

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