Preparation and catalytic studies of bis(halogeno) dioxomolybdenum(VI)-diimine complexes

Željko Petrovski[a], Martyn Pillinger[b], Anabela A. Valente[b], Isabel S. Gonçalves[b,*], Alan Hazell[c], Carlos C. Romão[a,**]

[a] *Instituto de Tecnologia Química e Biológica da Universidade Nova de Lisboa, Quinta do Marquês, EAN, Apt. 127, 2781-901 Oeiras, Portugal*
[b] *Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago, 3810-193 Aveiro, Portugal*
[c] *Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

Abstract

Dioxomolybdenum(VI) complexes of the type MoO_2X_2L containing ethylenediimine ligands were prepared in good yield by reaction of $MoO_2X_2(THF)_2$ (X = Cl, Br) with the bidentate ligands $Ph_2C=NCH_2CH_2N=CPh_2$ (PBED) or $PhCH=NCH_2CH_2N=CHPh$ (BED). The crystal structure of $MoO_2Br_2(BED)$ was determined by X-ray diffraction. The dichloro complexes were active as catalysts for the reaction of cyclooctene with *tert*-butyl hydroperoxide (TBHP) at 55 °C yielding epoxycyclooctane as the only product up to 7 h after the start of the reaction. The highest initial activity was obtained with $MoO_2Cl_2(BED)$ (63 mol mol_{Mo}^{-1} h^{-1}). Other olefins were also tested, and activities decreased in the order cyclooctene > cyclododecene > (*R*)-(+)-limonene > cyclohexene > *trans*-2-octene > 1-octene. The dibromo complexes exhibited much lower activities than the dichloro complexes for the epoxidation of cyclooctene.
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1. Introduction

Epoxides are important organic intermediates since they undergo ring-opening reactions with a variety of reagents to give mono- or bi-functional organic products [1,2]. In general, epoxides can be prepared by the reaction of olefins with hydrogen peroxide or alkylhydroperoxides, catalyzed by transition metal complexes [3,4]. Some examples of recently explored catalysts are iron-phenanthroline [5], ruthenium-porphyrin [6] and manganese-mep [7] complexes. Molybdenum catalysts are also very versatile in olefin epoxidation [3,8]. In the homogeneous phase (Arco and Halcon processes), molybdenum catalysts are commercially applied to the production of propylene oxide using

alkyl hydroperoxides as oxidants [9,10]. One of the preferred oxygen sources is *tert*-butyl hydroperoxide (TBHP), partly because it is environment-friendly, not very corrosive or hazardous, and the by-product of the reaction, *tert*-butyl alcohol, can be easily separated and recycled for use in other industrial processes [8]. In recent years, a good number of oxomolybdenum(VI) complexes with the *cis*-MoO_2 fragment have been studied as homogeneous catalysts for the reaction of olefins with TBHP, including compounds of the type $(\eta^5$-$C_5R_5)MoO_2Cl$ [11,12], $MoO_2X_2(L^1)_n$ [13–23], $MoO_2X(L^2)_m(L^1)_n$ and $MoO_2(L^2)_m(L^1)_n$ [24–27] (X = F, Cl, Br, CH_3; L = mono or bidentate neutral (L^1) or anionic (L^2) N-, O-, S-ligand). Important properties, such as the solubility of the complex and the Lewis acidity of the metal centre can be fine-tuned by variation of X and L. With regard to the choice of neutral ligand L^1, bidentate imines are particularly attractive since they allow considerable scope for the variation of steric and electronic properties. Dioxo-

molybdenum(VI) complexes with polypyridyl ligands, such as bipyridine and bipyrimidine are rather sluggish catalysts of low general activity [16–18,21]. Better results have been obtained using substituted 1,4-R_2-diazabutadienes as supporting ligands [17,18,22]. In an effort to further examine the effects of ligands in dioxomolybdenum(VI) complexes, we now wish to report on the catalytic properties of a new family of complexes containing ethylenediimine ligands.

2. Experimental

2.1. Materials and methods

Solvents were dried by standard procedures, distilled under nitrogen and stored over molecular sieves. Ethylenediamine was dried over sodium and distilled prior to use. d_6-DMSO and C_6D_6 were used as received. Microanalyses were performed at the ITQB (C. Almeida). IR spectra were recorded on a Mattson 7000 FT-IR spectrometer using KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-300 spectrometer. The ligand *N,N'*-bis(α-phenylbenzylidene)ethylenediamine ($Ph_2C=NCH_2CH_2N=CPh_2$) [28] and one catalyst precursor, the solvent adduct $MoO_2Br_2(MeCN)_2$ [16] were obtained as described previously. The dioxomolybdenum(VI) complexes were prepared and handled under nitrogen.

2.2. N,N'-bis(benzylidene)ethylenediamine

Freshly distilled benzaldehyde (5 mL, 49.5 mmol) was added dropwise to ethylenediamine (1.65 mL, 24.8 mmol) under nitrogen and at room temperature. The reaction mixture was vigorously stirred and cooled in an ice bath. After 10 min benzene was added and the water was removed by azeotropic distillation. The remaining solvent was removed under reduced pressure and the solid residue dried to give the ligand as a yellow solid in quantitative yield. Found: C, 80.82; H, 6.70; N, 11.44. $C_{16}H_{16}N_2$ (236.32) requires C, 81.32; H, 6.83; N, 11.85%. IR (KBr): $\nu = 3079$, 3056, 3026, 2912, 2848, 1642 (s), 1579, 1448, 1373, 1313, 1284, 1219, 1024, 988, 753 (s), 692 (s), 515 cm^{-1}. ^1H NMR (300 MHz, C_6D_6, Si(CH$_3$)$_4$, 20 °C): $\delta = 8.02$ (s, 2H), 7.71 (m, 4H), 7.06 (m, 6H), 3.89 (s, 4H) ppm. ^{13}C NMR (75.4 MHz, C_6D_6, Si(CH$_3$)$_4$, 20 °C): $\delta = 161.83$, 137.02, 130.46, 128.61, 128.43, 62.10 ppm. DEPT (75.4 MHz, C_6D_6, Si(CH$_3$)$_4$, 20 °C): $\delta = 161.83$ (+), 130.47 (+), 128.61 (+), 128.43 (+), 62.11 (−) ppm.

2.3. MoO$_2$Cl$_2$(Ph$_2$C=NCH$_2$CH$_2$N=CPh$_2$) (1)

A solution of *N,N'*-bis(α-phenylbenzylidene)ethylenediamine (247 mg, 0.64 mmol) in THF (5 mL) was added dropwise to a solution of MoO_2Cl_2 (127 mg, 0.64 mmol) in THF (5 mL). After stirring for 20 min at room temperature, the greenish-yellow solution was filtered and evaporated

to dryness. The solid product was washed with hexane and dried in vacuum (0.36 g, 96%). Found: C, 56.88; H, 4.64; N, 4.59. $C_{28}H_{24}N_2O_2Cl_2Mo$ (587.35) requires C, 57.26; H, 4.12; N, 4.77%. IR (KBr): $\nu = 3063$, 2977, 2873, 1658, 1627, 1596, 1446, 1318, 1278, 1174, 942, 917, 765, 703 cm^{-1}. Selected Raman: 3063 s, 1633 m, 1596 vs, 1000 s, 952 m, 915 m, 218 w, 205 m cm^{-1}. ^1H NMR (300 MHz, CD$_3$CN, Si(CH$_3$)$_4$, 20 °C): $\delta = 7.79$–7.41 (m, 20H, C$_6$H$_5$), 4.09 (s, 4H, CH$_2$) ppm. ^{13}C NMR (75.4 MHz, d_6-DMSO, Si(CH$_3$)$_4$, 20 °C): $\delta = 137.16$, 132.83, 130.55, 129.72, 128.99, 128.72, 128.44, 128.24, 127.42 (all phenyl-C), 50.21 (CH$_2$) ppm.

2.4. MoO$_2$Br$_2$(Ph$_2$C=NCH$_2$CH$_2$N=CPh$_2$) (2)

A solution of *N,N'*-bis(α-phenylbenzylidene)ethylenediamine (288 mg, 0.74 mmol) in THF (5 mL) was added dropwise to a solution of $MoO_2Br_2(MeCN)_2$ (274 mg, 0.74 mmol) in THF (5 mL). After stirring for 30 min at room temperature, the dark solution was filtered and evaporated to dryness. The solid product was washed with hexane and dried in vacuum (0.41 g, 81%). Found: C, 49.82; H, 3.56; N, 4.39. $C_{28}H_{24}N_2O_2Br_2Mo$ (676.25) requires C, 49.73; H, 3.58; N, 4.14%. IR (KBr): $\nu = 3051$, 2970, 2839, 1624, 1593, 1503, 1445, 1334, 1278, 1167, 1109, 955, 918, 785, 766, 703, 639 cm^{-1}. ^1H NMR (300 MHz, CD$_3$CN, Si(CH$_3$)$_4$, 20 °C): $\delta = 7.83$–7.44 (m, 20H, C$_6$H$_5$), 4.14 (s, 4H, CH$_2$) ppm. ^{13}C NMR (75.4 MHz, d_6-DMSO, Si(CH$_3$)$_4$, 20 °C): $\delta = 136.46$, 132.12, 129.87, 129.02, 128.29, 128.01, 127.72, 127.54, 126.72 (all phenyl-C), 49.53 (CH$_2$) ppm.

2.5. MoO$_2$Cl$_2$(PhCH=NCH$_2$CH$_2$N=CHPh) (3)

A solution of *N,N'*-bis(benzylidene)ethylenediamine (637 mg, 2.70 mmol) in THF (10 mL) was added dropwise to a solution of MoO_2Cl_2 (512 mg, 2.57 mmol) in THF (10 mL). After stirring for 30 min at room temperature the yellow solution was filtered and evaporated to dryness. The solid product was washed with hexane and dried in vacuum (1.10 g, 94%). Found: C, 44.20; H, 3.71; N, 6.56. $C_{16}H_{16}N_2O_2Cl_2Mo$ (435.16) requires C, 44.16; H, 3.71; N, 6.44%. IR (KBr): $\nu = 2972$, 2863, 2736, 1703, 1675, 1624, 1598, 1490, 1439, 1311, 1228, 1204, 1036, 999, 928, 905, 850, 828, 756, 715, 701, 684, 650 cm^{-1}. Selected Raman: 3060 m, 1633 vs, 1596 vs, 1000 s, 928 s, 915 m, 234 m, 208 s cm^{-1}. ^1H NMR (300 MHz, CD$_3$CN, Si(CH$_3$)$_4$, 20 °C): $\delta = 8.57$ (s, 2H, CH=N), 8.06–7.52 (m, 10H, C$_6$H$_5$), 4.15 (s, 4H, CH$_2$) ppm. ^{13}C NMR (75.4 MHz, CD$_3$CN, Si(CH$_3$)$_4$, 20 °C): $\delta = 169.41$ (CH=N), 135.43, 131.36, 130.52, 129.89, 129.60 (all phenyl-C), 55.33, 52.28 (CH$_2$) ppm.

2.6. MoO$_2$Br$_2$(PhCH=N−CH$_2$CH$_2$−N=CHPh) (4)

A solution of *N,N'*-bis(benzylidene)ethylenediamine (226 mg, 0.95 mmol) in THF (5 mL) was added dropwise to a solution of $MoO_2Br_2(MeCN)_2$ (362 mg, 0.98 mmol) in THF (5 mL). The solution turned bright yellow imme-

diately and some precipitation occurred. After stirring for 30 min at room temperature the solvent was removed to give a solid residue, which was washed with hexane and dried in vacuum (0.50 g, 94%). Found: C, 36.36; H, 3.13; N, 5.35. $C_{16}H_{16}N_2O_2Br_2Mo$ (524.06) requires C, 36.67; H, 3.08; N, 5.35%. IR (KBr): $\nu = 2962, 2781, 1670, 1615, 1597, 1576, 1450, 1434, 1356, 1316, 1228, 1195, 1042, 999, 935, 926, 902, 850, 754, 715, 700, 690 \text{ cm}^{-1}$. ^{1}H NMR (300 MHz, CD_3CN, $Si(CH_3)_4$, 20 °C): $\delta = 8.43, 8.40$ (2s, 2H total, CH=N), 7.87–7.62 (m, 10H, C_6H_5), 4.59, 4.26 (2s, 4H total, CH_2) ppm. ^{13}C NMR (75.4 MHz, d_6-DMSO, $Si(CH_3)_4$, 20 °C): $\delta = 163.96$ (CH=N), 134.74, 131.34, 131.33, 129.63, 129.09, 128.79, 128.51 (all phenyl-C), 56.67 (CH_2) ppm.

2.7. Crystal structure determination of 4

Crystals of complex **4** suitable for X-ray crystallography were prepared as follows: a solution of N,N'-bis(benzylidene)ethylenediamine (134 mg, 0.57 mmol) in MeCN (5 mL) was added dropwise to a solution of MoO_2Br_2 (163 mg, 0.57 mmol) in MeCN (5 mL). Precipitation occurred immediately. The reaction mixture was heated to reflux to dissolve the solid. Heating and stirring were then stopped and the solution was left to cool slowly overnight. Precipitation of dark crystals occurred together with some powder. The solution and the powder were decanted from the crystals and, as the crystals were not regular monocrystals, the whole procedure was repeated again, re-dissolving them in hot acetonitrile. After cooling overnight dark monocrystals were formed. The structure was determined at 100 K using graphite monochromatized radiation. Data were collected on a Siemens SMART diffractometer [29]. Crystal data and experimental parameters are presented in Table 1. The data were corrected for Lorentz-polarization effects and for absorption [29]. The structure was solved by direct methods using SIR97 [30] and refined by least-squares techniques using programs from the KRYSTAL package [31]. Hydrogen atoms were kept fixed in calculated positions with C–H = 0.95 Å and with isotropic displacement factors 20% larger than U_{eq} for the atoms to which they were bonded. Atomic scattering factors were taken from elsewhere [32].

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 240874. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK. Fax: (international) +44 1223/336 033; E-mail address: deposit@ccdc.cam.ac.uk).

2.8. Catalysis

The liquid-phase catalytic epoxidations were carried out at 55 °C under air (atmospheric pressure) in a reaction vessel equipped with a magnetic stirrer and immersed in a thermostated oil bath. A 1% molar ratio of complex/substrate and a substrate/oxidant molar ratio of 0.65 (TBHP, 5.5 M

in decane) were used. The course of the reaction was monitored using a gas chromatograph (Varian 3800) equipped with a capillary column (SPB-5, 20 m × 0.25 mm) and a flame ionization detector. The products were identified by gas chromatography–mass spectrometry (HP 5890 Series II GC; HP 5970 Series Mass Selective Detector) using He as carrier gas.

3. Results and discussion

3.1. Synthesis and characterization

The ligands N,N'-bis(α-phenylbenzylidene)ethylenediamine (PBED) and N,N'-bis(benzylidene)ethylenediamine (BED) were prepared in quantitative yields by the condensation of the appropriate ketone or aldehyde with ethylenediamine. Four dioxomolybdenum(VI) complexes with the general formula MoO_2X_2L (**1–4**, Plate 1) were then obtained by simple ligand exchange with the solvent adducts

Table 1
Crystal data and structure refinement for $MoO_2Br_2(BED)$ (**4**)

Molecular formulation	$MoO_2Br_2(C_{16}H_{16}N_2)$
Empirical formula	$C_{16}H_{16}Br_2MoN_2O_2$
Formula weight	524.06
Crystal system	Hexagonal
Space group	$P3_1$
a (Å)	7.7240(3)
b (Å)	7.7240(3)
c (Å)	25.40(2)
γ (°)	120.0
V (Å)^3	1314.4(1)
Z	3
D_{calc} (g cm^{-1})	1.986
T (K)	100
Reflections collected	17224
Independent (R_{int})	4993(0.030)
Observed ($I > 3\sigma I$)	4789
R indices[a] ($I > 3\sigma I$) $R1$	0.032
$wR1$	0.043
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.6(2), −1.6(2)

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $\quad wR1 = \left(\sum ||F_o| - |F_c|| \right)^2 / \sum w |F_o^2|^{1/2}$, $\quad w = 1/\{\left(\left(\sigma F_o^2 \right) + B + (1 + A) F_o^2 \right)^{1/2} - |F_o|\}^2$, $A = 0.03$, $B = 2.0$.

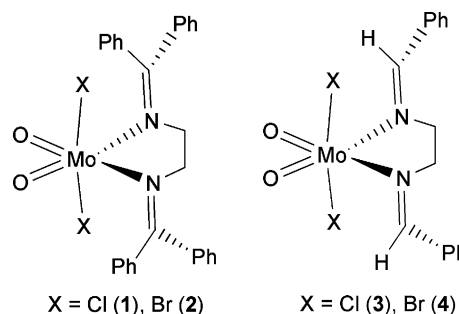X = Cl (**1**), Br (**2**)   X = Cl (**3**), Br (**4**)

Plate 1.

$MoO_2X_2S_2$ (X = Cl, Br; S = THF, MeCN). Unlike the solvent adducts, which are air- and moisture-sensitive, complexes **1**–**4** are air-stable solids. The complexes display their symmetric and asymmetric IR stretching vibrations for the *cis*-dioxo unit at 941 ± 13 and $910 \pm 8\,cm^{-1}$, respectively, in agreement with other complexes of this type containing 1,4-diazabutadiene ligands [17]. In the Raman spectra of the dichloro complexes **1** and **3**, a medium–strong band at about $205\,cm^{-1}$ is assigned to the MoN_2 symmetric stretch, while a slightly weaker band at higher frequency ($234\,cm^{-1}$ for **3**) is probably due to the $MoCl_2$ symmetric stretch [21]. NMR spectroscopy indicates compound **4** to be an isomeric mixture. Thus, the ^1H NMR spectrum shows two singlets for the bridging methylene protons at $\delta = 4.26$ and 4.59 (4H total), and two singlets for the imine protons at $\delta = 8.40$ and 8.43 (2H total). By contrast, the dichloro complex **3** only exhibited one singlet for the methylene protons and one singlet for the imine protons. It is tempting to assign the signals displayed by compound **4** to symmetrical *trans*, *trans* and *cis*, *cis* complexes. Since the starting ligand was geometrically pure, isomerization could be promoted by complexation as a result of unfavorable steric interactions between the aryl groups of the ligand and the MoO_2Br_2 fragment. A molybdenum tetracarbonyl complex bearing the ligand BED was also reported to an isomeric mixture [33].

The crystal structure of $MoO_2Br_2(PhCH=NCH_2CH_2N=CHPh)$ (**4**) was determined by X-ray diffraction. Selected bond distances and angles are listed in Table 2. The compound is monomeric (Fig. 1). Molybdenum is coordinated to the nitrogen atoms of the bis(benzylidene)ethylenediamine group, $Mo-N = 2.310(2)$ and $2.316(2)$ Å, two oxygen atoms with $Mo-O = 1.732(3)$ and $1.750(3)$ Å, and two bromine atoms with $Mo-Br = 2.529(1)$ and $2.532(1)$ Å. These bond distances are similar to those for $MoO_2Br_2L_2$ complexes
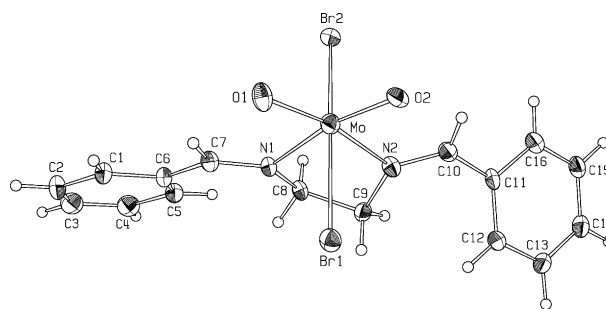

Fig. 1. Molecular structure of $MoO_2Br_2(PhCH=N-CH_2CH_2-N=CHPh)$ (**4**).

where $L_2 = 2,2'$-bipyridine [21], $2,2'$-bipyrimidine [16], bis(acetonitrile) [16], and $4,4'$-di(*tert*-butyl)-2,2'-bipyridine [34]. In the refined crystal structure, both phenyl groups were found to be *cis* to the bridging methylene groups (as shown in Plate 1).

The coordination polyhedra in these compounds are distorted octahedra with $O-Mo-O > O-Mo-N \sim O-Mo-Br > N-Mo-N$, the distortions arising partly from repulsion between two double bonds being greater than that between a double and a single bond which again is greater than that between two single bonds. Angles involving the large bromine atoms are larger than similar angles without bromine so that $O-Mo-Br > O-Br-N$. $N-Mo-N$ angles for the bipyridyl-like ligands are in the range $68.8(1)$–$69.6(2)°$. The corresponding angle in the acetonitrile complex, where there is no constraint on the $N \cdots N$ distance, is larger ($75.75(9)°$), while complex **4** has an intermediate $N-Mo-N$ angle of $71.1(1)°$. The $O-Mo-O$ angles show the reverse effect: $106.8(2)$–$107.0(1)°$ for the aromatic ligands, $104.4(1)°$ for the acetonitrile complex, and $105.3(2)°$ for the bis(benzylidene)ethylenediamine complex **4**. Thus, it is possible to modify the $O-Mo-O$ angle by choosing the appropriate ligand.

3.2. Catalytic tests

All the compounds were tested as catalysts for the reaction of cyclooctene with TBHP at 55 °C. The TBHP was used as a 5.5 M solution in decane. After its addition, homogeneous conditions were obtained. The complexes **1** and **3** are active for the reaction, yielding epoxycyclooctane as the only product up to 7 h after the start of the reaction (Fig. 2). Complex **3** is more active than **1**. The lower activity of **1** may be due to greater steric constraints caused by the extra two phenyl groups present in the metal coordination sphere. Compared with other complexes of the type MoO_2X_2L, complex **3** is on the low end of the activity scale for cyclooctene epoxidation. The initial activity of **3**, calculated after 15 min, is 63 mol $mol_{Mo}^{-1}\,h^{-1}$. This is comparable with the activities exhibited by dioxomolybdenum(VI) complexes containing symmetrical bipyridine and bipyrimidine ligands [21]. Dichloro dioxomolybdenum(VI)–diazabutadiene complexes gener-

Table 2
Selected bond distances (Å) and angles (°) for **4**

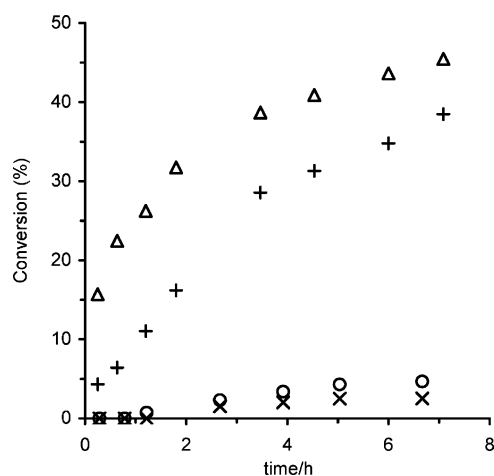|	
Mo−N1	2.316(2)
Mo−N2	2.310(2)
Mo−O1	1.732(3)
Mo−O2	1.750(3)
Mo−Br1	2.532(1)
Mo−Br2	2.529(1)
N1−Mo−N2	71.1(1)
N1−Mo−O1	90.9(1)
N1−Mo−O2	163.9(1)
N1−Mo−Br1	81.69(9)
N1−Mo−Br2	80.92(9)
N2−Mo−O1	161.9(1)
N2−Mo−O2	92.7(1)
N2−Mo−Br1	81.61(9)
N2−Mo−Br2	80.78(9)
O1−Mo−O2	105.3(2)
O1−Mo−Br1	97.5(1)
O1−Mo−Br2	95.4(1)
O2−Mo−Br1	96.2(1)
O2−Mo−Br2	96.9(1)
Br1−Mo−Br2	158.44(2)

Fig. 2. Conversion profiles for the epoxidation of cyclooctene with TBHP at 55 °C in the presence of the dioxomolybdenum(VI) complexes **1** (+), **2** (×), **3** (△) and **4** (O).
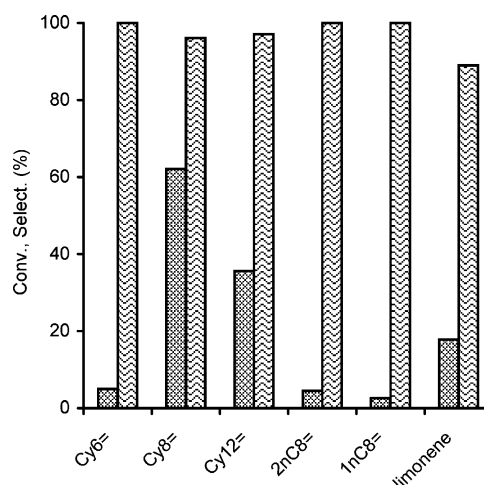

Fig. 3. Olefin conversion at 24 h (diamonds) and selectivity to the corresponding epoxide (waves) with TBHP at 55 °C using complex **3** (cyclohexene = Cy6=; cyclooctene = Cy8=; cyclododecene = Cy12=; *trans*-2-octene = 2nC8=; 1-octene = 1nC8=; (*R*)-(+)-limonene = limonene).

ally exhibit higher activities (under very similar reaction conditions), for example 175 mol mol$_{Mo}^{-1}$ h^{-1} for the complex MoO$_2$Cl$_2${*p*-tolyl(CH$_3$DAB)} [*p*-tolyl(CH$_3$DAB) = *N*,*N*-*p*-tolyl-2,3-dimethyl-1,4-diazabutadiene] [22]. With substrate:catalyst ratios of about 100, the highest turnover frequencies reported for MoO$_2$Cl$_2$L complexes are about 600 mol mol$_{Mo}^{-1}$ h^{-1} [21].

The kinetic profiles of **1** and **3** are typical of complexes of the type MoO$_2$Cl$_2$L (L = bidentate Lewis base N-ligand) reported previously. After a comparatively rapid increase in the product yield in the early stages (especially for **3**), the reaction slows down considerably during the course of the catalytic run. Experimental and theoretical investigations on these types of complexes have indicated that the first step of the catalytic cycle involves the transfer of a TBHP proton to the terminal oxygen atom of one of the Mo=O groups and coordination of $^-$OO-*t*-Bu to the Lewis acidic metal centre (Eq. (1)), leading to the formation of an intermediate Mo^{VI} η^1-alkylperoxo species (MoLy) [21]. The peroxide becomes activated for oxygen transfer to the olefin resulting in the formation of the epoxide and *tert*-butanol (*t*BuOH) (Eq. (2)), a by-product, which competes with TBHP for coordination to the metal centre (leading to the formation of MoLz, Eq. (3)), thus retarding the reaction. Under the applied reaction conditions, the dichloro species **1** and **3** showed much higher activity than their dibromo analogues **2** and **4**, respectively, which give a maximum conversion of 5% at 7 h. This is a common observation for MoO$_2$X$_2$L complexes and can be ascribed to steric and/or electronic effects. Previous studies with similar MoO$_2$X$_2$L complexes (L = 4,4′-dialkyl-2,2′-bipyridine) have confirmed that in the presence of excess TBHP, neither of the ligands X nor L are lost [21].

$$\text{TBHP} + \text{MoLx} \rightleftharpoons \text{MoLy} \tag{1}$$

$$\text{MoLy} + \text{Cy} \rightarrow \text{MoLx} + \text{CyO} + t\text{BuOH} \tag{2}$$

$$\text{MoLx} + t\text{BuOH} \rightleftharpoons \text{MoLz} \tag{3}$$

Fig. 3 shows the results obtained at 24 h for the catalytic system containing complex **3**, TBHP and several different linear and cyclic olefins. The catalytic activity tends to decrease as the olefin becomes less substituted (less reactive): cyclooctene > cyclododecene > (*R*)-(+)-limonene > cyclohexene > *trans*-2-octene > 1-octene. For cyclooctene, the selectivity is no longer 100% (as it was at 7 h), due to consecutive epoxide ring opening, leading to the formation of the corresponding diol. Nucleophilic ring opening of 1,2-epoxides in aqueous medium is possible in the presence of Lewis acids. Hence the small quantities of 1,2-diol formed as a by-product may arise from water present in the TBHP solution (up to 4%). Complex **1** yielded nearly double the amount of diol than **3**. Most likely the extra two electron-attracting aromatic groups present in **1** enhance the Lewis acidity provided by the Mo^{VI} metal centre, such that it suffices for converting the epoxide into the diol. The oxidation of the more bulky substrate, cyclododecene, is slower than that of cyclooctene, possibly due to steric constraints, and produces the epoxide as the main product with 97% selectivity at 36% conversion, the diol being the minor product. In the case of (*R*)-(+)-limonene, regioselectivity is highly in favor of the epoxidation of the internal cyclic double bond, yielding limonene oxide and 8,9-epoxy-*p*-menth-1-ene in a molar ratio of 8. The conversion of cyclohexene or linear olefins is less than 5% after 24 h and the corresponding epoxides are the only products formed.

The catalyst **3** was used in a second reaction cycle of 24 h by charging an extra 1.8 mmol substrate and TBHP after 24 h of cyclooctene epoxidation (Fig. 4). The reaction continued and the rate increased again at the beginning of the second cycle. According to the above mechanism for molybdenum-catalyzed epoxidations with TBHP, this may
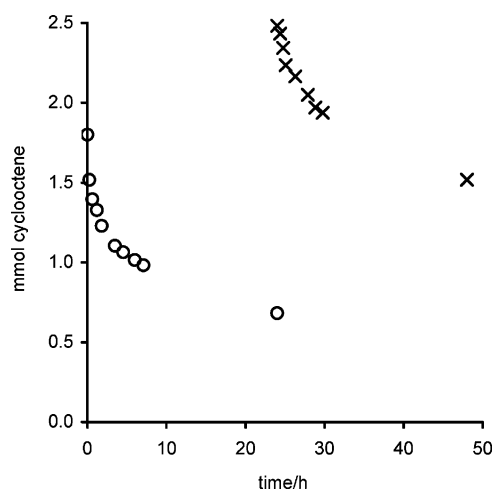
Fig. 4. Kinetics of the oxidation of cyclooctene with TBHP in the presence of complex **3** for the first (O) and second (×) runs at 55 °C.

be due to the addition of TBHP together with the substrate at 24 h, thereby increasing the TBHP/tBuOH molar ratio and as a result reducing the extent of the autoretardation effect [21,22].

4. Conclusion

In the present work, the family of complexes with the general formula MoO_2X_2L has been expanded to include species containing diimine ligands derived from ethylenediamine. The catalytic behavior of these complexes for the epoxidation of olefins is strongly dependent on the nature of the halide substituent. Quite good results were obtained for the dichloro complex $MoO_2Cl_2(PhCH=NCH_2CH_2N=CHPh)$. The catalytic activity is comparable with that exhibited by MoO_2X_2L complexes containing symmetrical bipyridyl ligands. Better results have, however, been obtained with complexes containing 1,4-R_2-diazabutadiene ligands. Nevertheless, the fact that the above complex is significantly more active than $MoO_2Cl_2(Ph_2C=NCH_2CH_2N=CPh_2)$ suggests that there is considerable scope for the improvement of catalytic results by variation of the substituents at the imine carbon atoms. The possibility to prepare enantioselective oxidation catalysts by using chiral substituents is currently under investigation in our laboratories.

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