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PEROXO AND ALKYLPEROXIDIC MOLYBDENUM(VI) COMPLEXES AS INTERMEDIATES IN THE EPOXIDATION OF OLEFINS BY ALKYL HYDROPEROXIDES

PATRICK CHAUMETTE, HUBERT MIMOUN *, LUCIEN SAUSSINE

Laboratoire d'Oxydation, Institut Français du Pétrole, 92506 Rueil-Malmaison (France)

JEAN FISCHER and ANDRE MITSCHLER

Laboratoire de Cristallochimie et Chimie Structurale, Université Louis Pasteur,
67070 Strasbourg Cédex (France)

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Summary

Novel oxoperoxomolybdenum(VI) complexes with the general formula $MoO(O_2)L_2X_2$ (III, L = DMF, HMPT) and $MoO(O_2)Cl(O{-}N)L$(IV, O–N = pyridin-2-carboxylate (Pic), 8-hydroxyquinolinate (Quin)) were prepared from the reaction of Ph_3COOH or H_2O_2 with the corresponding *cis*-dioxo complexes. In the reaction with Ph_3COOH both oxygen atoms of the peroxo moiety were found, by ^{18}O labeling experiments, to come from the hydroperoxide. The X-ray crystal structure of $MoO(O_2)Cl(Pic)(HMPT)$ revealed a bipyramidal pentagonal surrounding with a rather short O–O distance (1.41 Å). Complexes III were found to be more reactive than $MoO(O_2)_2$,HMPT for the epoxidation of olefins (oxidative cleavage products are consecutively formed) but react by the same cyclic peroxymetalation mechanism. The absence of reaction in the case of complexes IV illustrates the necessity for the metal to possess an equatorial releasable coordination site adjacent to the peroxo group for the oxygen transfer to occur. Catalytic oxidation of olefins using Ph_3COOH gave a selectivity in oxygenated products very different from that using t-BuOOH, and ^{18}O labeling studies showed that alkyl-peroxidic rather than peroxo species are intermediates in this latter reaction. The mechanism of epoxidation of olefins by alkyl hydroperoxides catalyzed by d^0 metal complexes is discussed.

Introduction

High-valent d^0 transition metal complexes, such as Mo^{VI}, V^V, Ti^{IV} are effective catalysts for the selective epoxidation of olefins by alkylhydroperoxides (eq. 1) [1].

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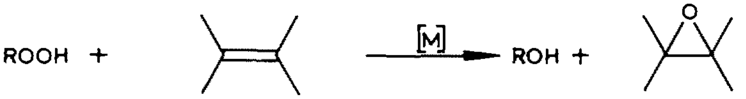
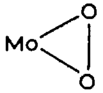


(1)

Although this reaction has been known since 1965 [2] and has been developed into a commercial process for the manufacture of propylene oxide by Halcon (M = Mo) [3] and by Shell (M = Ti) [4], its mechanism still remains a matter of controversy. Three important questions have not yet received definitive answers.

1. What is the nature of the reactive intermediate? Is it a peroxo, **1**, or alkylperoxidic, **2**, species [5]? Peroxo complexes such as **3** are firmly established as selective epoxidation reagents [6] and have been isolated from the reaction of alkylhydroperoxides with molybdenum compounds (under fairly drastic conditions) [7]. However ^{18}O labeling studies favor alkylperoxidic **2** complexes as the active species [8].



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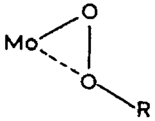

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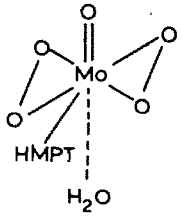
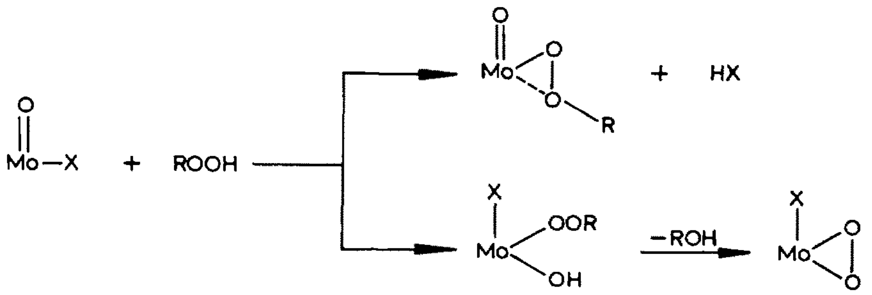


(**3**)

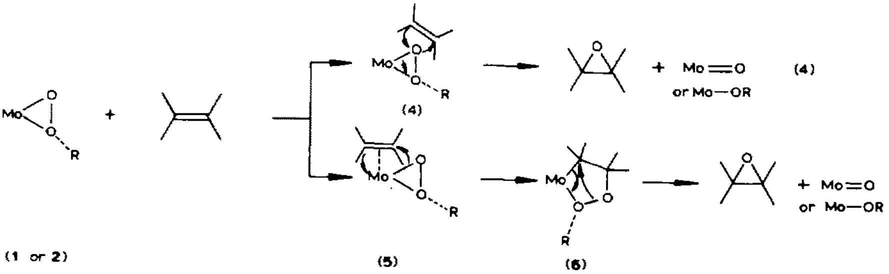
2. What is the mode of formation of akyl-peroxidic species? Anion exchange on the metal (eq. 2) or nucleophilic attack on the molybdenum–oxo bond Mo=O (eq. 3)? *N*,*N*-Dialkylhydroxylamines, the nitrogen analogues of alkyl hydroperoxides, react according to eq. 2 (e.g. $MoO_2Cl_2 \rightarrow MoO_2(ONR_2)_2$) [9], but H_2O_2 reacts according to eq. 3 to give the peroxo species [10].



(2)

(3)

3. What is the mode of oxygen transfer from peroxo and alkyl-peroxidic species to olefins? External nucleophilic attack of the olefin on the "electrophilic" oxygen atom bound to the metal as in **4** (eq. 4) [8,11] or complexation-insertion of the olefin to form the five-membered peroxometallocycle **6**, a process referred to as peroxymetalation [10,12].



(4)

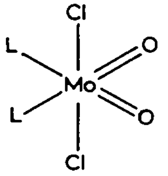
(5)

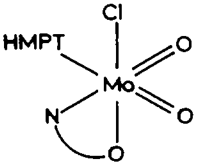
In the work described below we attempted to isolate and characterize molybdenum peroxidic complexes from the reaction of alkyl hydroperoxides with *cis*-dioxomolybdenum(VI) complexes, and studied their stoichiometric reactivity toward olefins compared with that in catalytic oxidation.

Results and discussion

1. Reaction of alkyl hydroperoxides with cis-dioxomolybdenum(VI) complexes. Synthesis and characterization of monoperoxo complexes from Ph_3COOH

cis-Dioxomolybdenum(VI) complexes $MoO_2Cl_2L_2$ (type I; L = DMF, HMPT) and $MoO_2Cl(O\text{-}N)L$ (type II; O–N = Pic, Quin; L = HMPT) were used as starting material. They are well-defined compounds, soluble in organic solvents, and generally good epoxidation catalysts [13]. An octahedral structure, with a *cis* arrangement of the two oxo bonds and the two neutral basic ligands, and a *trans* arrangement of the two anionic ligands, was established by X-ray structure crystallography [14].

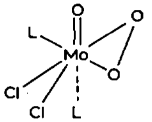

(Ia, L = DMF ;
Ib, L = HMPT)

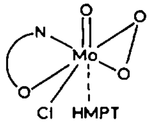

(IIa ,O—N = Pic ;
IIb ,O—N= Quin)

In the infrared, these complexes exhibit the two characteristic *cis*-dioxo vibrations in the range 900–950 cm^{-1}, and the ligand absorptions are modified by coordination to the metal [15,16].

As alkyl hydroperoxides, we used t-BuOOH (**7**), $PhMe_2COOH$ (**8**), Ph_3SnOOH (**9**), and Ph_3COOH (**10**), in the pure anhydrous form.

The addition of an excess of **7**, **8**, or **9** to a solution of the complexes I or II in CH_2Cl_2 gave an immediate yellow color, but all attempts to isolate the resulting complex were unsuccessful, and the starting compound was recovered unchanged. However, addition of one equivalent of Ph_3COOH gave an orange coloration, and new monoperoxo complexes of types III (from type I) and IV (from type II) were isolated pure and in good yield after precipitation with diethyl ether.


(IIIa ; L = DMF;
IIIb; L = HMPT)


(IVa,O—N = Pic ;
IVb,O—N = Quin)

These yellow-orange complexes were characterized by elemental analysis, infrared, NMR, active oxygen cerimetric titration (see Experimental section) and X-ray crystallography (for IVa). Table 1 lists the most important infrared characteristics of monoperoxo complexes III and IV, namely the $\nu(Mo{=}O)$ vibration at 930–960 cm^{-1} and the three C_{2v} peroxo vibrations at ca. 920, 550 and 600 cm^{-1}.

The conversion of dioxomolybdenum(VI) into oxoperoxo complexes can be

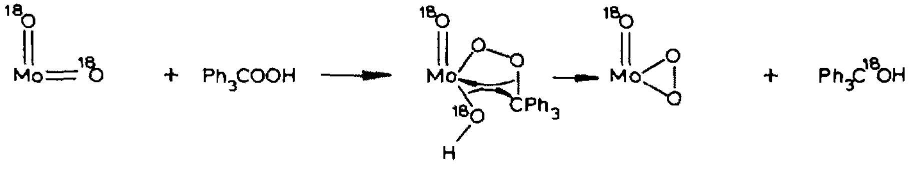
TABLE 1

MONOPEROXOMOLYBDENUM(VI) COMPLEXES

Complex	Infrared vibrations (cm^{-1})[a]			
	$\nu(Mo{=}O)$	$\nu(O{-}O)$	$\nu(Mo\langle^{O}_{O}|)_{s,as}$	$\nu(Y{-}O)$[b] $\Delta\nu$
$MoO(O_2)Cl_2$,2DMF (IIIa)	955	920	545,590	1189 (−21)
$MoO(O_2)Cl_2$,2HMPT (IIIb)	960	920	550,600	1645 (−27)
$MoO(O_2)Cl$,Pic,HMPT (IVa)	950	920	550,600	1188 (−22)
$MoO(O_2)Cl$,Quin,HMPT (IVb)	947	920	550,600	1189 (−21)

[a] KBr disc. [b] Y = C(DMF), P(HMPT).

represented as in eq. 6. The stoichiometry of this reaction was confirmed for Ib. The



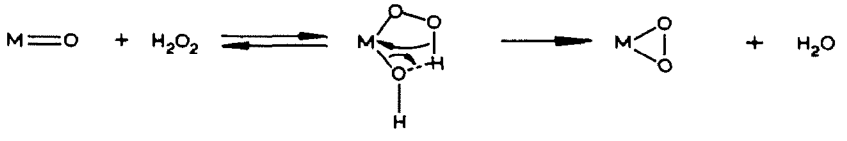
(6)

(11) (12)

peroxo complex IIIb was obtained in 86% yield, and triphenylmethanol (**12**) was isolated in 95% yield.

The mechanism of this reaction has been determined by ^{18}O labeling studies. Addition of an excess of $H_2{}^{18}O$ (99% isotope purity) to Ia in CH_2Cl_2 resulted in the formation of an ^{18}O labeled compound (infrared determination) containing 50% $Mo^{16}O^{16}O$, 35% $Mo^{16}O^{18}O$ and 15% $Mo^{18}O^{18}O$ [17]. The reaction of one equivalent of Ph_3COOH with this labeled dioxo complex gave the peroxo complex IIIa, unlabeled on the peroxo oxygen atoms (no displacement in infrared of the $\nu(O{-}O)$ peroxo vibration at 920 cm^{-1}) and 28% labeled Ph_3COH (GLC-MS determination), corresponding to 86% incorporation of available ^{18}O in the initial complex. This therefore indicates that both oxygen atoms of the peroxo group come from the hydroperoxide, while one labeled oxo oxygen atom is incorporated into Ph_3COH. Thus, addition of Ph_3COOH must have occurred at the metal–oxo bond, forming the hydroxo alkylperoxo species **11**. The decomposition of **11** is facilitated by the stability of the cation Ph_3C^+ and by its good leaving group character.

A similar mechanism was proposed to explain the formation of peroxo complexes from hydrogen peroxide and d^0 metal oxo compounds through the hydroxo hydroperoxide (**13**) (eq. 7) [10,18].



(7)

(**13**)

Addition of one equivalent of H_2O_2 to complexes I and II in CH_2Cl_2 gave the monoperoxo complexes III and IV, but in lower yields than from Ph_3COOH. Addition of an excess H_2O_2 to Ib gave the well-known diperoxo complex $MoO(O_2)_2$,HMPT,H_2O (3).

The absence of formation of monoperoxo complexes from the reaction of hydroperoxides **7**, **8**, and **9**, can, in the light of eq. 3, probably be attributed to the lower stability of the cation R in t-butyl- and cumyl-hydroperoxide.

2. *X-ray crystal structure of* $MoO(O_2)(Pic)$*,HMPT (IVa)*

Atomic positional parameters, with corresponding esd's estimated from the least squares inverse matrix and thermal parameters are shown in Table 2. Bonds lengths and bond angles appear in Table 3. Tables of observed and calculated structure factor amplitudes and thermal parameters are available from the authors.

The coordination polyhedron of molybdenum is a deformed pentagonal bipyramid (Fig. 1). The five equatorial coordination positions are occupied by the O(4)–O(5) peroxo group, a chlorine atom, and the nitrogen and oxygen atoms of the picolinate moiety. The two apical positions are occupied by the terminal oxygen atom O(3) and the atom O(6) of HMPT. This geometry is normal compared to that of the diperoxo complexes **3** [19] and $[MoO(O_2)_2(Pic)]^-$ H^+ (**14**) [20] and the monoperoxo complex $MoO(O_2)$(dipic),H_2O (**15**) [20]. The oxo Mo–O(3) and the peroxo Mo–O distances are in the range of those found in the above-cited complexes, but the O(4)–O(5) bond is significantly shorter (1.41 compared with 1.45–1.50 Å). This explains the higher frequency of the infrared ν(O–O) bond (920 cm^{-1} compared with 870–900 cm^{-1}). The Mo–O(HMPT) bond is longer than in complex **3**, owing to the *trans* effect of the apical oxo group. The picolinate ligand is planar within experimental error.

Attempts to isolate single crystals of the type III complexes failed, but the coordination polyhedron III (*cis*-arrangement of the anionic positions in the equatorial plane) can be suggested by analogy with the structure of IVa and that of the diperoxo complexes.

3. *Oxidation of olefins by monoperoxomolybdenum(VI) complexes*

The stoichiometric oxidation of olefins by peroxo complexes III and IV was

(*Continued on p. 299*)

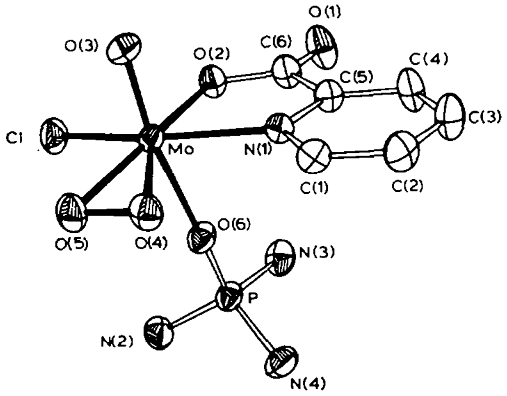


Fig. 1. ORTEP plot on one molecule of $MoO(O_2)Cl(Pic)(HMPT)$. Ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity.

TABLE 2

TABLE OF POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

(Estimated standard deviations in the least significant digits are shown in parentheses; the form of the anisotropic thermal parameter is: $T = \exp[-(B_{11}h^{*2} + B_{22}k^{*2} + B_{33}l^{*2} + B_{12}h^{*}k + b_{13}h^{*}l + B_{23}k^{*}l]$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo	0.70938(2)	0.51469(4)	0.38926(2)	0.00381(1)	0.01514(6)	0.00290(1)	−0.00060(4)	0.00123(2)	−0.00123(4)
Cl	0.65546(7)	0.7901(2)	0.38275(8)	0.00550(5)	0.0179(2)	0.00681(5)	0.0033(2)	0.00238(9)	−0.0040(2)
P	0.66084(9)	0.5030(1)	0.18138(7)	0.00518(5)	0.0204(2)	0.00290(4)	0.0044(2)	0.00017(8)	−0.0011(1)
O(1)	0.9239(2)	0.6136(4)	0.2841(2)	0.0049(1)	0.0197(6)	0.0103(2)	−0.0018(5)	0.0063(2)	0.0062(6)
O(2)	0.8087(2)	0.6302(3)	0.3453(2)	0.0041(1)	0.0133(4)	0.0062(1)	−0.0010(4)	0.0025(2)	−0.0010(4)
O(3)	0.7479(2)	0.5272(4)	0.4808(2)	0.0063(2)	0.0294(7)	0.0034(1)	0.0012(6)	−0.0005(2)	−0.0046(4)
O(4)	0.6422(2)	0.3216(4)	0.3994(2)	0.0048(1)	0.0218(6)	0.0056(1)	−0.0030(5)	0.0026(2)	0.0010(5)
O(5)	0.5967(2)	0.4697(4)	0.4070(2)	0.0049(1)	0.0247(7)	0.0062(2)	−0.0010(5)	0.0037(2)	0.0002(5)
O(6)	0.6798(2)	0.4905(4)	0.2671(2)	0.0059(2)	0.0203(6)	0.0031(1)	0.0043(4)	−0.0001(2)	−0.0013(4)
N(1)	0.7950(2)	0.3146(4)	0.3605(2)	0.0039(1)	0.0142(5)	0.0035(1)	−0.0005(4)	0.0009(2)	0.0006(4)
N(2)	0.5849(3)	0.6258(6)	0.1643(2)	0.0056(2)	0.0315(9)	0.0041(2)	0.0079(7)	−0.0004(3)	0.0005(6)
N(3)	0.7372(3)	0.5828(6)	0.1367(2)	0.0072(2)	0.0263(8)	0.0042(1)	0.0049(8)	0.0026(3)	0.0034(6)
N(4)	0.6419(3)	0.3190(6)	0.1467(2)	0.0074(2)	0.0272(8)	0.0049(2)	0.0049(7)	−0.0022(3)	−0.0085(6)
C(1)	0.7843(3)	0.1500(5)	0.3719(3)	0.0051(2)	0.0148(7)	0.0043(2)	−0.0025(6)	0.0012(3)	0.0023(6)
C(2)	0.8391(4)	0.0350(6)	0.3485(4)	0.0066(2)	0.0122(6)	0.0064(2)	0.0021(7)	0.0007(4)	0.0023(7)
C(3)	0.9069(3)	0.0860(7)	0.3135(4)	0.0067(2)	0.0185(9)	0.0078(3)	0.0050(8)	0.0046(4)	−0.0005(8)
C(4)	0.9189(3)	0.2549(6)	0.3014(3)	0.0047(2)	0.0179(8)	0.0086(3)	0.0036(7)	0.0052(4)	0.0023(8)
C(5)	0.8624(3)	0.3638(5)	0.3268(3)	0.0045(2)	0.0157(7)	0.0044(2)	0.0004(6)	0.0014(3)	0.0015(6)
C(6)	0.8680(3)	0.5502(6)	0.3171(3)	0.0044(2)	0.0158(7)	0.0061(2)	−0.0011(6)	0.0021(3)	0.0002(7)

C(7)	0.5140(3)	0.6185(8)	0.2129(3)	0.0056(2)	0.0325(12)	0.0060(2)	0.0080(9)	0.0006(4)	−0.0015(10)
C(8)	0.5680(5)	0.7149(11)	0.0911(4)	0.0097(4)	0.0488(18)	0.0059(3)	0.0169(13)	0.0000(5)	0.0081(11)
C(9)	0.7734(5)	0.5130(10)	0.0712(5)	0.0087(4)	0.0444(21)	0.0088(4)	0.0075(12)	0.0082(6)	−0.0031(12)
C(10)	0.7679(5)	0.7462(8)	0.1601(3)	0.0114(4)	0.0290(12)	0.0062(2)	−0.0040(12)	0.0041(5)	0.0115(8)
C(11)	0.5823(5)	0.2795(11)	0.0874(4)	0.0089(4)	0.0461(17)	0.0069(3)	−0.0043(14)	−0.0010(6)	−0.0156(11)
C(12)	0.6885(5)	0.1750(8)	0.1727(4)	0.0125(4)	0.0253(11)	0.0080(3)	0.0109(11)	−0.0056(6)	−0.0132(9)

Atom	x	y	z	$B(\text{Å}^2)$	Atom	x	y	z	$B(\text{Å}^2)$
HC(1)	0.7373(0)	0.1130(0)	0.3973(0)	5.0000(0)	H(2)C(9)	0.7945(0)	0.4064(0)	0.0847(0)	5.0000(0)
HC(2)	0.8295(0)	−0.0805(0)	0.3564(0)	5.0000(0)	H(3)C(9)	0.7342(0)	0.5040(0)	0.0293(0)	5.0000(0)
HC(3)	0.9461(0)	0.0071(0)	0.2979(0)	5.0000(0)	H(1)C(10)	0.8119(0)	0.7755(0)	0.1287(0)	5.0000(0)
HC(4)	0.9655(0)	0.2938(0)	0.2759(0)	5.0000(0)	H(2)C(10)	0.7255(0)	0.8263(0)	0.1526(0)	5.0000(0)
H(1)C(7)	0.4751(0)	0.6990(0)	0.1949(0)	5.0000(0)	H(3)C(10)	0.7858(0)	0.7439(0)	0.2135(0)	5.0000(0)
H(2)C(7)	0.4906(0)	0.5107(0)	0.2095(0)	5.0000(0)	H(1)C(11)	0.5833(0)	0.1636(0)	0.0774(0)	5.0000(0)
H(3)C(7)	0.5306(0)	0.6417(0)	0.2658(0)	5.0000(0)	H(2)C(11)	0.5302(0)	0.3108(0)	0.1043(0)	5.0000(0)
H(1)C(8)	0.5197(0)	0.7797(0)	0.0951(0)	5.0000(0)	H(3)C(11)	0.5935(0)	0.3389(0)	0.0410(0)	5.0000(0)
H(2)C(8)	0.6121(0)	0.7866(0)	0.0810(0)	5.0000(0)	H(1)C(12)	0.6682(0)	0.0787(0)	0.1460(0)	5.0000(0)
H(3)C(8)	0.5603(0)	0.6376(0)	0.0494(0)	5.0000(0)	H(2)C(12)	0.7439(0)	0.1907(0)	0.1628(0)	5.0000(0)
H(1)C(9)	0.8167(0)	0.5835(0)	0.0563(0)	5.0000(0)	H(3)C(12)	0.6826(0)	0.1604(0)	0.2277(0)	5.0000(0)
C(S1)	0.9576(8)	0.246(2)	0.0413(8)	8.2(3)	C(S5)	0.9795(8)	0.303(2)	0.0426(7)	7.6(3)
C(S2)	1.0515(12)	0.356(3)	0.4844(11)	12.8(6)	C(S6)	1.0066(12)	−0.096(3)	−0.0120(10)	12.0(5)
C(S3)	0.9971(10)	0.785(3)	0.4855(9)	10.4(4)	C(S7)	1.0555(9)	0.037(2)	−0.0340(9)	7.8(3)
C(S4)	0.9288(14)	0.106(3)	0.0551(13)	13.5(6)					

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (°) WITH e.s.d. FOR IVa

Distances	Å	Angles	(°)
Mo–C(1)	2.383(1)	N(1)–Mo–O(2)	73.7(1)
Mo–N(1)	2.207(3)	N(1)–Mo–C(1)	154.8(1)
Mo–O(2)	2.051(3)	O(4)–Mo–O(5)	43.2(1)
Mo–O(3)	1.663(3)	C(1)–Mo–O(5)	79.8(1)
Mo–O(4)	1.916(3)	N(1)–Mo–O(4)	78.9(1)
Mo–O(5)	1.927(3)	O(3)–Mo–N(1)	92.0(1)
Mo–O(6)	2.130(3)	O(3)–Mo–C(1)	96.4(1)
O(4)–O(5)	1.414(5)	O(3)–Mo–O(4)	99.2(1)
		O(3)–Mo–O(5)	101.0(1)
		O(6)–Mo–N(1)	80.4(1)
		O(6)–Mo–C(1)	88.3(1)
		O(4)–O(5)–Mo	68.0(2)
		O(5)–O(4)–Mo	68.8(2)

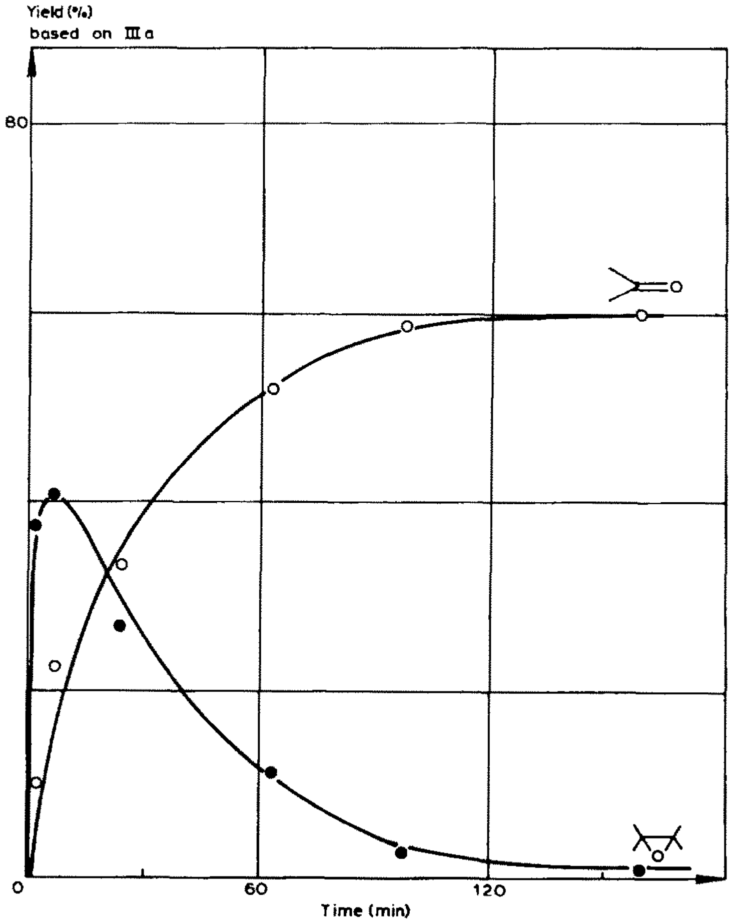
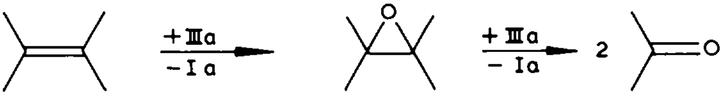


Fig. 2. Oxidation of 2,3-dimethyl-2-butene by IIIa. Température, 0°C, [IIIa] 0.02 *M*; solvent, CH_2Cl_2; olefin/complex = 40.

carried out at room temperature under nitrogen in CH_2Cl_2 or $C_2H_4Cl_2$. Only type III complexes were found to be reactive. Figure 2 shows a typical plot of 2,3-epoxy-2,3-dimethylbutane and acetone formation vs. time when 2,3-dimethyl-2-butene was oxidized by IIIa at 0°C in CH_2Cl_2. The epoxide was mainly formed at the beginning of the reaction, but progressively disappeared at the expense of the oxidative cleavage compound. The solution initially orange became colorless at the end of the reaction, but then became blue upon standing for a long time. The *cis*-dioxomolybdenum(VI) precursor Ia was obtained in quantitative amounts from the colorless solution by precipitation with diethyl ether. A control experiment showed that the reaction of IIIb or IIIa with epoxides such as styrene oxide and *trans*-stilbene oxide under the same conditions mainly produced benzaldehyde [21]. Equation 8 summarizes the sequence of these reactions.



(8)

Table 4 lists some representative results obtained when various olefins were stoichiometrically oxidized by complexes of types III and IV. The reactivity of monoperoxo complexes III appears to be very similar to that of $MoO(O_2)_2$,HMPT [6,22], and can be summarized as follows:

1. Only complexes III having an adjacent coplanar coordination site occupied by a monodendate basic ligand were found to be reactive. Complexes IV, **14** and **15**, which do not fulfill this condition, were completely inactive even when the reaction was carried out at 60°C for 4 h. Further, IIIa was found to be more reactive than IIIb (Entries 10 and 11), due to the greater donor effect of HMPT compared to that of DMF ($D_N(SbCl_5) = 38.8$ vs.26.6) [23].

2. The reactivity of olefins increases with their nucleophilic nature in the order: tetrasubstituted > trisubstituted > disubstituted > monosubstituted. Olefins containing phenyl substituents, such as α- and β-methylstyrene, gave more oxidative cleavage products than the aliphatic ones.

3. The epoxidation of olefins is completely stereoselective. Thus *cis*-2-butene gave only *cis*-epoxide and *trans*-2-butene *trans*-epoxide.

4. The reaction is strongly inhibited by basic ligands such as DMF and HMPT. Addition of 1.5 equivalent of DMF at the beginning of the epoxidation of tetramethylethylene by IIIa resulted in a ca. twofold decrease of the reaction rate (Fig. 3).

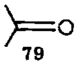
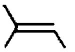
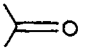
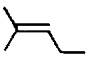
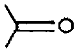
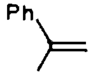
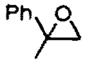
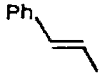
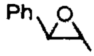
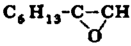
5. As for complex **3**, the reaction of IIIa is first order in the concentration of the complex (Fig. 3). The rate constant k' obtained from the first-order plot of log [IIIa] vs. time (UV determination by measuring the decrease of the characteristic absorption at 395 nm) was found to be 5 to 10 fold greater than that of complex **3** (Table 5). This is probably due to the more electrophilic nature of molybdenum in IIIa as a result of the presence of the two chloride ligands.

The characteristics of the epoxidation of olefins by complexes III, notwithstanding their greater reactivity, are similar to those by complex **3** and can therefore be interpreted in terms of the same mechanism, as shown in Scheme 1.

The first, rate-determining, step consists of the exchange of the equatorial ligand L by the olefin, to give **16** in which the olefin–metal interaction is through a pure Lewis base–Lewis acid bond. Insertion of the olefin into the metal–oxygen bond

TABLE 4

OXIDATION OF OLEFINS[a]

Entry	Complex	Time (min)	Olefin	Products[b]	Yield (%)[c]	
						
1	IIIa	20		14	79	
2	IIIa[d]	20		38	52	
3	IIIa[e]	20		32	32	
4	IVa	240		0	0	
						MeCHO
5	IIIa	90		40	25	24
						EtCHO
6	IIIb	90		43	25	25
						MeCHO
7	IIIb	240		16	0	2
						MeCHO
8	IIIb	240		0	15	2
					PhCOMe	
9	IIa	240		20	37	
					PhCHO	MeCHO
10	IIIa	150		0	43	n.d.
11	IIIb	150		5	18	n.d.
			$C_6H_{13}CH{=}CH_2$		 $C_6H_{13}\text{-}C\text{—}CH_2$ (O)	$C_6H_{13}CHO$
12	IIIb	360			10	0

[a] Reaction conditions: temperature, 20°C; complex, 0.03 *M*; olefin/complex = 40; solvent, CH_2Cl_2. [b] Identified by GLC-MS coupling. [c] GLC determination using various internal standards. [d] Conditions are the same as above except olefin/complex = 100. [e] temperature, 0°C; olefin/complex = 40.

(π–σ rearrangement or internal 1,3-dipolar cycloaddition) results in the transient formation of the five-membered peroxometallacycle **17**, which decomposes to the epoxide and the dioxo complex **18**. Addition of ligand L to **18** regenerates the more stable *cis*-dioxo complex I, which was isolated.

The reactivity of complexes III and the absence of reactivity of complexes IV, **14** and **15** allows us to specify the stereochemistry (depicted in Scheme 1) of the mechanism previously proposed for $MoO(O_2)_2$,HMPT [6]. The presence on the metal of an equatorial, adjacent and releasable coordination site appears necessary for the oxygen transfer reaction to occur. The mechanism of eq. 4 (external attack of the olefin on the peroxo oxygen atom) can therefore be ruled out on this basis. Owing to the close similarity of the molybdenum peroxo complexes in their configuration, their peroxidic nature, and the O–O distances, an external attack

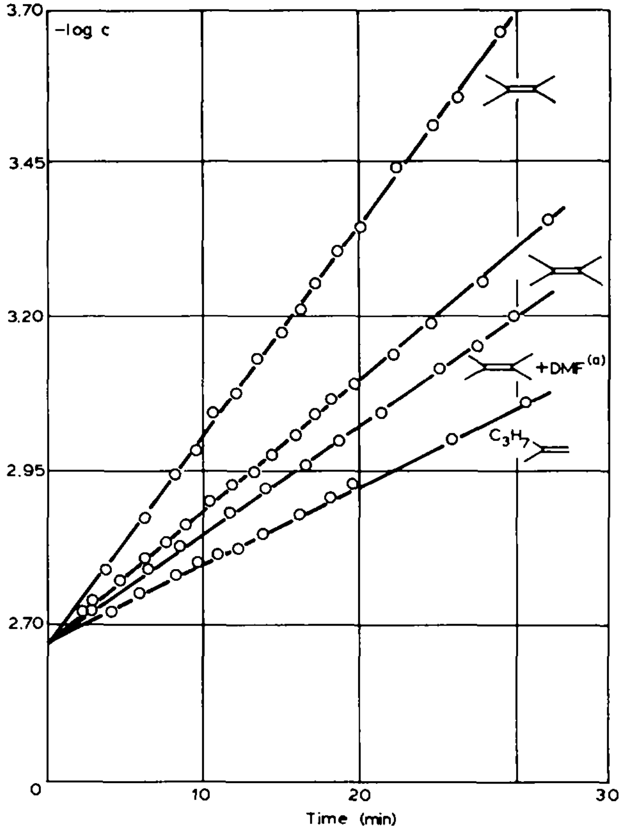
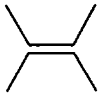
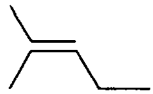


Fig. 3. Oxidation of olefins by IIIa. First order plot of log [IIIa] vs. time. temperature, 20°C: [IIIa] 2.1×10^{-3} M; olefin/complex = 40; solvent, CH_2Cl_2. [a] DMF = 3.5×10^{-3} M.

TABLE 5

FIRST-ORDER RATE CONSTANTS k' (s^{-1}) FOR EPOXIDATION BY IIIa[a] and 3[b]

Olefin	10^5 k' (IIIa)	10^5 k' (3)
	63.9	12.3
	42.2	5.2
	25.0	2.

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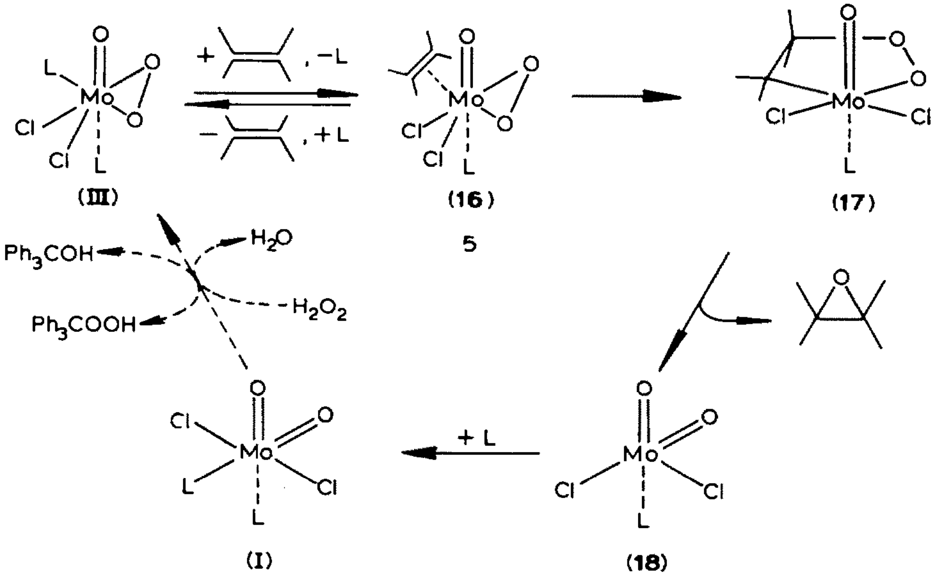
[a] Calculated for olefin concentration of 8.4×10^{-2} M at 20°C in CH_2Cl_2, see experimental conditions in Fig. 3. [b] Taken from references [6] and [22].

SCHEME I



should not be influenced by the nature and the arrangement of the ligands in the coordination sphere of the metal.

4. Catalytic epoxidation of olefins

The use of t-BuOOH or Ph_3COOH as the oxygen source in the epoxidation of olefins catalyzed by *cis*-dioxomolybdenum(VI) complexes resulted in a markedly different selectivity. Figure 4 shows a typical plot of 2,3-epoxy-2-methylpentane, acetone and propionaldehyde formation vs. time when 2-methyl-2-pentene was oxidized by t-BuOOH (**7**) and Ph_3COOH (**10**) in the presence of catalytic amounts of Ia under the same conditions. In the former case, the solution remained pale yellow. Epoxide was formed with a 98% selectivity, and only traces of cleavage compounds were observed. The use of Ph_3COOH resulted in a much lower epoxide selectivity and the formation of a significant amount of cleavage products. During the reaction, the solution remained orange and a precipitate appeared, which was identified as the dialkylperoxide $Ph_3COOCPh_3$ **18** (50% yield based on **10**). Triphenylmethanol **12** was isolated in ca. 50% yield (based on **10**) at the end of the reaction.

A more pronounced difference of selectivity was observed in the epoxidation of *trans*-β-methylstyrene by **7** and **10** catalyzed by Ia, as shown in Fig. 5. Reaction with **7** gave the epoxide as the major product, while use of **10** mainly gave oxidative cleavage products, as previously shown for the stoicheiometric oxidation of *trans*-β-methylstyrene by IIIa. The use of H_2O_2 as oxidant also resulted in the formation of oxidative cleavage products. In order to prevent the formation of diperoxo complexes, one equivalent of H_2O_2 (70% purity) was added all once to a solution of Ia in a CH_2Cl_2/*trans*-β methylstyrene solution (olefin/Ia = 70). This resulted in an orange coloration which progressively disappeared, and in the formation of benzaldehyde in 40% yield. The same operation was repeated ten times and the accumulated products found to be mainly those resulting from cleavage.

This therefore strongly suggests that peroxo complexes are involved as reactive

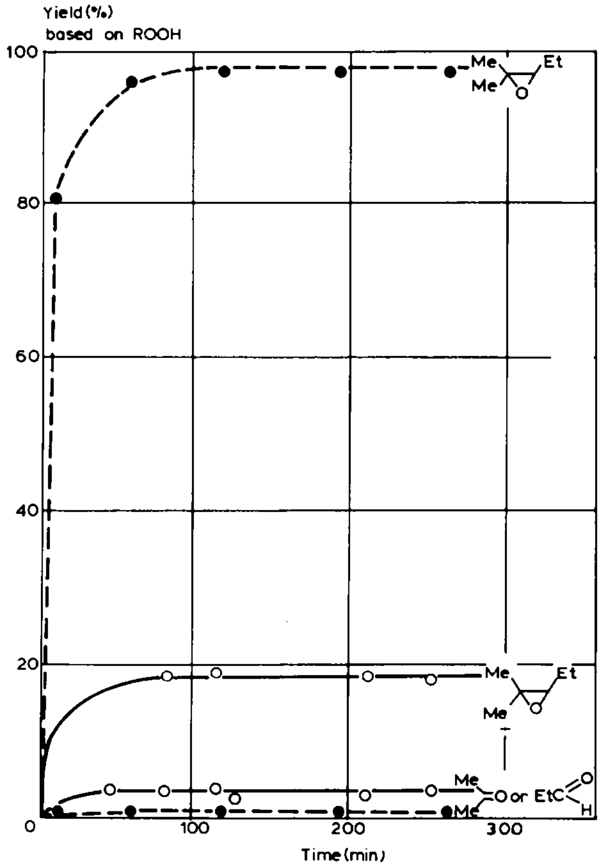
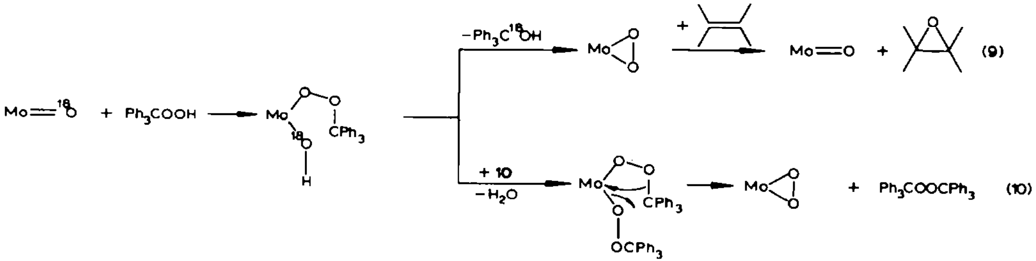


Fig. 4. Oxidation of 2-methyl-2-pentene by t-BuOOH or Ph_3COOH catalysed by Ia. ● t-BuOOH, ○ Ph_3COOH; [Ia] 0.02 *M*; solvent, CH_2Cl_2: temperature, 20°C; ROOH/complex = 20; olefin/complex = 70.

intermediates in the oxidation of olefins by Ph_3COOH and H_2O_2, while t-BuOOH produces a non-isolated different reactive species.

This difference between Ph_3COOH and t-BuOOH has also been illustrated by ^{18}O labeling experiments. Addition of one equivalent of Ph_3COOH to ^{18}O-labeled complex Ia (see above for the ^{18}O content) in the presence of excess 2-methyl-2-pentene at 20°C ($C_2H_4Cl_2$, olefin/Ia = 20) resulted in the formation of unlabeled epoxide and Ph_3COH containing 80% of the available ^{18}O content of Ia. Equations 9



(11)

(19)

(18)

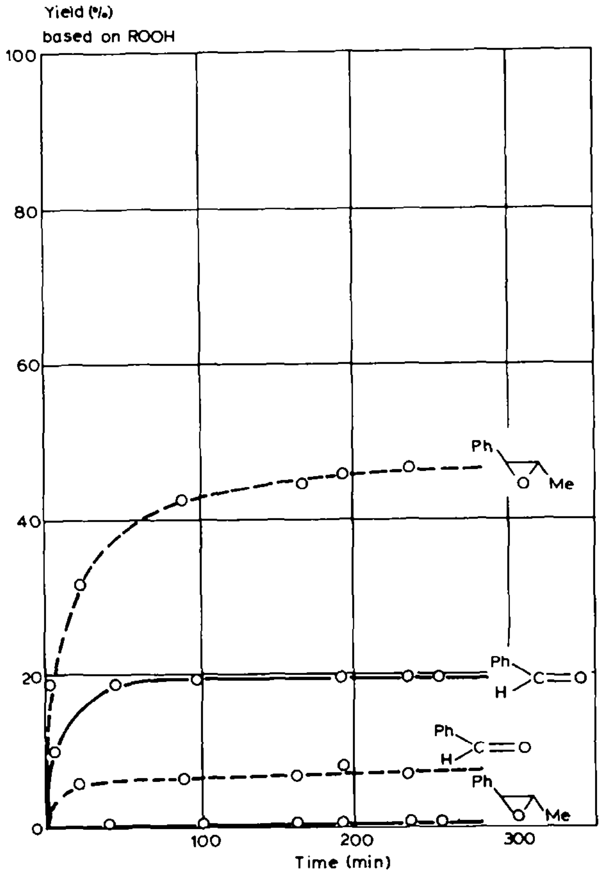


Fig. 5. Oxidation of *trans-β*-methyl styrene by t-BuOOH or Ph_3COOH catalyzed by Ia. [Ia] 0.02 *M*; solvent, CH_2Cl_2; temperature, 20°C; olefin/complex = 70; ROOH/complex = 20. — — — t-BuOOH, —— Ph_3COOH.

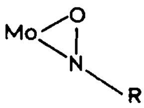
and 10 illustrate these reactions. The formation of the dialkylperoxide **18** observed when excess of **10** was used, can be explained by the decomposition of **19** resulting from the exchange of the hydroxo group in **11** by **10**.

A similar ^{18}O-labeling experiment carried out with t-BuOOH gave a completely different result. Addition of one equivalent of t-BuOOH to the ^{18}O-labeled complex Ia in the presence of excess cyclohexene (20°C, CH_2Cl_2, olefin/Ia = 20) resulted in the formation of unlabeled epoxycyclohexane and unlabeled t-BuOH. This confirms the results of the previous ^{18}O labeling experiment carried out by Sharpless on the epoxidation of cyclododecene by t-BuOOH in the presence of $Mo(CO)_6$ and $H_2{}^{18}O$ [8], which led to the conclusion that peroxo complexes are not formed in this reaction, and that the active species involves an intact OO-t-Bu group.

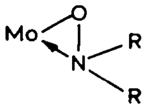
5. Discussion

Despite many attempts in our and other laboratories, reactive alkylperoxidic molybdenum(VI) complexes have so far never been isolated. However, on the basis of the extensive available experimental data [1] we can make the following suggestions for the mechanism of the molybdenum-catalyzed epoxidation of olefins by alkyl hydroperoxides.

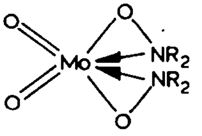
a. Alkylperoxidic molybdenum(VI) species probably result from anion exchange between the metal and ROOH (eq. 2) rather than from nucleophilic attack on the oxo bond (eq. 3). Hydroxylamine and its *N*-alkyl derivatives are isoelectronic with H_2O_2 and give O,N-coordinated d^0 metallooxaziridine (**20**), formally analogous to peroxo complexes [24]. N,N-Substituted hydroxylamines, which are the nitrogen analogues of alkyl hydroperoxides, give O,N-coordinated *N,N*-dialkylhydroxylamino complexes (**21**) [9,25] which can be considered as representative of d^0 alkyl peroxidic species. Among these complexes, $MoO_2(ONEt_2)_2$ (**22**) obtained from the reaction of Et_2NOH with *cis*-dioxomolybdenum(VI) complexes [9], is reminiscent of reactive $MoO_2(OOR)_2$ (**23**) or $MoO_2(OOR)Z$ species (Z = anionic ligand)



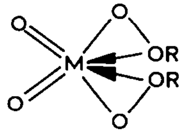
(20)



(21)



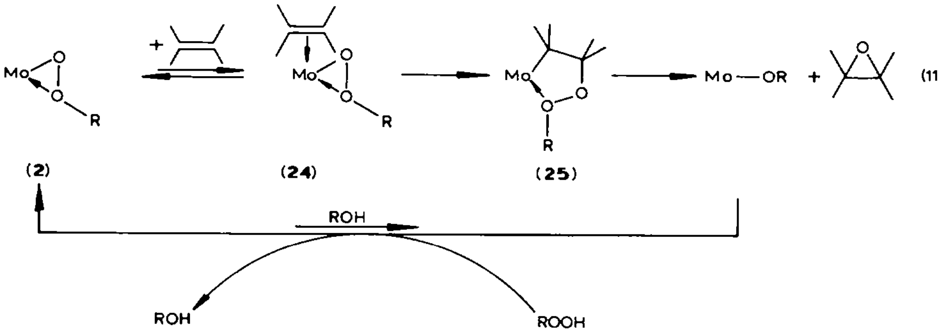
(22)



(23)

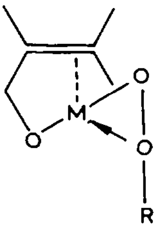
It is noteworthy that *cis*-dioxomolybdenum(VI) diolates, which could be formed in the reaction of epoxides (or diols) with **23**, were isolated and characterized by Sheldon at the end of the catalytic reaction in all cases studied whatever the nature of the molybdenum compound used [26]. The induction period, and even the absence of activity of several molybdenum complexes bearing strongly bound ligands [13] may be due to the difficulty of the displacement of the anionic ligands on the metal by the hydroperoxide.

b. The pseudocyclic peroxymetalation mechanism shown in eq. 11 satisfactorily accounts for most of the experimental data in catalytic epoxidation by alkyl hydroperoxides [10,12,27].



Coordination of the olefin to the metal is shown by the increase in the epoxidation rate with the nucleophilic nature of the olefin [1b], and by the strong inhibition of the reaction by basic ligands and solvents which compete with the olefins for vacant sites on the metal [28].

Taking account of the probable side-on O,O-coordination of the alkyl-peroxidic group on the metal and the analogy between *O,O*-alkyl-peroxidic and *O,N*-dialkylhydroxylamino complexes, the low catalytic activity of vanadium and titanium complexes for the catalytic epoxidation of non-activated olefins can be explained. The presumed *O,O*-coordinated alkylperoxidic intermediates $VO(OOR)_3$ or $V_2O_3(OOR)_4$ (similar to $V_2O_3(ONEt_2)_4$ [9,25]) and $Ti(OOR)_4$ (similar to $Ti(ONEt_2)_4$) [29] are coordinatively saturated and cannot bind non-activated olefins. However, allylic alcohols are particularly suitable substrates with both vanadium [1e,30] and titanium [31] catalysts, since they can displace OOR groups on the metal by forming complexes such as **26**, and are epoxidized with a very high stereo- and enantio-selectivity. It is noteworthy that the bidendated bis(hydroxamato)peroxomolybdenum(VI) complexes $MoO(O_2)(PhCON(Ph)O)_2$ are inactive toward unactivated olefins, but react easily with allylic alcohols [33].



(26)

The very high selectivity of d^0 metal-catalyzed epoxidation of olefins strongly supports the existence of the strained metallocyclic intermediate **25**. The mechanism of eq. 11 is consistent with that of similar selective oxidation, such as ketonization of olefins by PdOOR complexes, and epoxidation of olefins by $B(OOR)_3$ species [33], and is another example of the wide range of selective oxidations by peroxidic reagents [27].

Conclusion

We have shown that the course of molybdenum(VI)-catalyzed epoxidation of olefins by hydroperoxides varies depending on whether the oxygen source is (a) H_2O_2 or Ph_3COOH or (b) t-BuOOH. With H_2O_2 or Ph_3COOH stable and reactive peroxo complexes have been isolated and shown to react according to the same mechanism as $MoO(O_2)_2$,HMPT. In the case of other alkyl hydroperoxides, such as t-BuOOH, no intermediate complexes could be isolated, but the ^{18}O-labeling experiments ruled out the possibility of peroxo intermediates, and favored the involvement of d^0 alkyl-peroxidic species.

Experimental

(a) Reagents

All chemicals were used as commercially supplied unless otherwise indicated. Chlorinated solvents were distilled from calcium chloride and stored in nitrogen. Olefins were passed through a column containing active alumina to remove peroxidic impurities, distilled over sodium, and stored under nitrogen. t-Butyl hydroperoxide was obtained with 90% purity by distillation of the commercial product (Trigonox A75). Cumyl hydroperoxide (80% purity) was purchased from Merck. Triphenylmethyl hydroperoxide [34] and triphenyltin hydroperoxide [35] were prepared by known procedures.

(b) Apparatus

Infrared spectra were recorded by a Perkin–Elmer Model 457, UV-visible spectra by a Perkin–Elmer Model 402, and NMR spectra by a Varian CFT 20. Products were identified by coupled GLC-MS (Kratos Model MS80) and comparison with the mass spectra of authentic samples.

(c) Preparation of cis-dioxomolybdenum(VI) complexes

Complexes Ia,Ib were synthesized by known procedures [14d] and gave satisfactory elemental analyses and infrared and NMR spectra.

Synthesis of $MoO_2Cl(Pic),HMPT$ (IIa). Picolinic acid (2.2 g, 18 m*M*) was added to a solution of MoO_2Cl_2,2HMPT (Ib, 10g, 18 m*M*) in CH_2Cl_2. After stirring at 20°C for 2 h and concentration of the solution, addition of diethyl ether resulted in the precipitation of a white complex IIa which was filtered off, washed with diethyl ether, and dried in vacuo. Yield 5.8 g (68%). Anal. Found: C, 31.56; H, 4.91; N. 12.7; O. 17.5; Cl, 7.82. $C_{12}H_{22}O_5N_4PClMo$ calcd.: C, 31.0; H. 4.74; N. 12.06; O, 17.22; Cl, 7.64%. NMR spectrum (CD_2Cl_2): δ 2.45, 2.60 (d, 18 H), 8.20–8.35 (m, 1H), 8.75–9.25 (m, 3H) ppm.

Synthesis of $MoO_2Cl(Quin),HMPT$ (IIb). This orange complex was obtained by the same procedure as IIa, except that 8-hydroxyquinoline was used as bidendate ligand. Yield: 79%. Anal. Found C, 36.1; H. 5.1; N, 12.0; O, 12.5; Cl, 7.7. $C_{15}H_{24}O_4N_4PClMo$ calcd.: C, 37.0; H, 4.93; N, 11.51; O, 13.16; Cl, 7.3%. NMR spectrum (CD_2Cl_2): δ 2.58, 2.74 (d, 18 H), 6.95–7.10 (m, 1H), 7.35–7.60 (m, 2H), 8.25–8.35 (m, 2H), 9.05–9.10 (m, 1H) ppm.

(d) Preparation of monoperoxomolybdenum(VI) complexes; synthesis of $MoO(O_2)Cl_2$,2DMF (IIIa)

To 1.86 g (5.4 m*M*) of complex Ia dissolved in 30 ml of CH_2Cl_2 was added Ph_3COOH (1.6 g, 5.62 m*M*). The resulting orange solution was concentrated after 30 min stirring. Addition of diethyl ether gave a precipitate of IIIa. Yield 70%. Anal. Found: C, 20.45; H. 3.8; N, 7.8; O, 22.05; $C_6H_{14}O_5N_2Cl_2Mo$ calcd.: C, 19.94; H, 3.88; N, 7.76; O, 22.16%. NMR (CD_2Cl_2): δ 3.10 (s, 3H), 3.3 (s, 3H), 8.45 (s, 1H) ppm. The same complex was obtained in 60% yield from the reaction of 1 eq. H_2O_2 (70%) with Ia under the same conditions.

Synthesis of $MoO(O_2)Cl_2$,2HMPT (IIIb). This complex was prepared from Ib by the same procedure as IIIa. Yield: from **10** 86%; from H_2O_2 58%. Anal. Found: C, 24.68; H, 6.28; N, 14.52; O, 13.91; P, 10.79; Cl, 11.99; O active (cerimetry), 2.73. $C_{12}H_{36}O_5N_6P_2Cl_2Mo$ calcd.: C, 25.13; H, 6.28; N, 14.66; O, 13.96; P, 10.82; Cl, 12.39; O active 2.78%. NMR (CD_2Cl_2): δ 2.54–2.70; 2.70–2.86; 2.74–2.90 (36H, HMPT) ppm.

Triphenylmethanol was recovered by concentration of the filtrate after separation of IIIb. Yield 95% (based on Ph_3COOH). Anal. Found: C, 87.7; H, 6.1; O, 6.2. $C_{19}H_{16}O$ calcd.: C, 87.8; H, 6.01; O, 6.32%. The infrared spectrum was identical to that of the commercial product.

Synthesis of $MoO(O_2)Cl(Pic),HMPT$ (IVa). This was prepared from IIa. Yield: from **10** 85%; from H_2O_2 68%. Anal. Found: C, 30.6; H, 4.58; N, 13.28; O, 19.45; Cl, 7.30; O active, 3.16. $C_{12}H_{22}O_6N_4PClMo$ calcd.: C, 30.0; H, 4.58; N, 11.65; O, 19.88; Cl, 7.39; O active, 3.33%. NMR (CD_2Cl_2): δ 2.29, 2.45; 2.54, 2.70 (18H, HMPT); 7.75–8.25 (m, 1H); 8.35–8.40 (m, 2H); 9.72–9.80 (m, 1H) ppm.

Synthesis of $MoO(O_2)Cl(Quin)HMPT$ (IVb). This complex was prepared from IIb by the same method. Yield: from **10** 85%; from H_2O_2 65%. Anal. Found: C, 36.2; H, 4.8; N, 10.9; O, 15.83; Cl, 7.13; O active, 3.12. $C_{15}H_{24}O_5N_4PClMo$ calcd.: C, 35.8; H, 4.78; N, 11.14; O, 15.92; Cl, 7.06; O active, 3.18%. NMR (CD_2Cl_2): δ 2.20, 2.35; 2.4, 2.55 (18H, HMPT); 7.20–7.9 (m, 1H); 8.2–8.6 (m, 2H); 9.10–9.15 (m, 2H); 10–10.05 (m, 1H).

(e) Oxidation procedures and product analysis

The olefins were oxidized in a small double-jacketed glass flask connected to a vacuum-nitrogen line. In a typical procedure olefin and solvent were added in N_2 to the complex, and the progress of the reaction was monitored by GLC analysis of aliquot samples. Different columns were used, depending on the analysis required: Column A (FFAP 10% on Chromosorb WAW 3m) and column B (DEGS 10% on Chromosorp WHP 4m). The oxygenated products were identified by GLC-MS coupling and comparison of the mass spectra with those of authentic samples.

For kinetic studies the stoechiometric oxidation of olefins by peroxo complexes IIIa, IIIb was followed spectrophotometrically utilizing the decrease in the characteristic absorption at 395 nm.

Ditritylperoxide **18** separated out of the catalytic oxidation of olefins by **10**. It was characterized by infrared and elemental analysis. Anal. Found: C, 87.76; H, 6.05; O, 6.86. $C_{38}H_{30}O_2$ calcd.: C, 88.03; H, 5.75; O, 6.18%.

(f) Labeling Studies

^{18}O-labeled complex Ia. Ia (0.4 g) was dissolved in 2 ml anhydrous CH_2Cl_2 in the presence of 150 μl of $H_2{}^{18}O$ (99% purity) and the mixture was stirred for 3 h. The labeled complex was recovered by evaporation of the solution. It contained 50%. $Mo^{16}O^{16}O$ (ν(Mo=O): 941 and 903 cm^{-1}), 35% $Mo^{16}O^{18}O$ (ν(Mo=O): 930 and 872 cm^{-1}) and 15% $Mo^{18}O^{18}O$ (ν(Mo=O): 903 and 860 cm^{-1}).

*Reaction of **10** with Ia (^{18}O).* **10** (55 mg, 0.2 mM) was added to 0.1 g of Ia. After 30 min precipitation with diethyl ether gave complex IIIa, which had ^{18}O labels only on the oxo group. IR: $\nu\left(\mathrm{Mo}\!\begin{smallmatrix}\diagup\mathrm{O}\\ \ \ |\\ \diagdown\mathrm{O}\end{smallmatrix}\right)$ 920, 550, 600 cm^{-1} (unchanged); ν(Mo=O): 907 cm^{-1} (-48 cm^{-1}). The filtrate was analyzed by GLC-MS for the tritanol ^{18}O content (SE52 2 m column), which was found to be 28% ($Ph_3C^{18}OH$ $m/e = 262$, molecular peak), corresponding to 86% of the available ^{18}O content of Ia.

*Epoxidation of 2-methyl-2-pentene by **10** catalyzed by labeled Ia.* The same experiment was carried out in the presence of a twenty fold excess of 2-methyl-2-pentene, and the product mixture was analyzed by GLC-MS (column B). Unlabeled epoxide was found ($m/e = 85$, $C_5H_9O^+$). Acetone ($m/e = 60$, molecular peak) and propanal ($m/e = 60$, mol. peak) contained 5% ^{18}O, probably due to exchange reactions. Ph_3COH was found to contain 27% ^{18}O ($m/e = 262$, mol. peak) corresponding to 83% of the available ^{18}O transferred from the dioxo Ia complex.

Epoxidation of cyclohexene by t-BuOOH catalyzed by labeled Ia. To 0.1 g ^{18}O-labeled Ia (0.18 mM) dissolved in $C_2H_4Cl_2$, were added 20 μl 90% t-BuOOH (0.18 mM) and 0.3 ml cyclohexene (2.96 mM). After one hour, the mixture was analyzed by GLC-MS and found to contain unlabeled t-BuOH ($m/e = 59$, mol. peak), and unlabeled epoxycyclohexane ($m/e = 98$, mol. peak).

X-ray experimental section

Suitable single crystals of IVa were obtained by slow evaporation of a chlorobenzene solution at 4°C. A systematic search in reciprocal space using A Philips PW 1100/16 automatic diffractometer showed that crystals of IVa belonged to the monoclinic system. The unit-cell dimensions and their standard deviations were obtained and refined at room temperature with Cu-K_α radiation (λ 1.5405 Å) by using 25 carefully selected reflections and the standard Philips software. Final results: $C_{12}H_{22}N_4O_6MoClP$ $0.5(C_6H_5Cl)$, mol. wt.: 537, a 16.447(6), b 8.028(3), c 17.086(7) Å, β 92.68(2)°, V 2253 Å^3, $Z = 4$, d_{calc} 1.538 g cm^{-3}, μ 75.49 cm^{-1}, $F(000) = 1092$, space group $P2_1/C$.

A spherical crystal with 0.26 mm mean diameter was sealed in a Lindemann glass capillary and mounted on a free rotation goniometer head. All quantitative data were obtained from a Philips PW1100/16 four circle automatic diffractometer, controlled by a P852 computer, using graphite monochromated radiation and standard software. The vertical and horizontal apertures in front of the scintillation counter were adjusted so as to minimize the back-ground counts without loss of net peak intensity at the 2σ level. The total scan width in the $\theta/2\theta$ flying step-scan used was $\Delta\omega = 1.20 + (\text{Cu-}K_{\alpha_1\text{-}\alpha_2}$ splitting) with a step width of 0.05 deg and a scan speed of 0.02 deg sec^{-1}. 3390 hkl and $hk\bar{l}$ reflections were recorded ($4° < \theta < 57°$). The resulting data-set was transfered to a PDP 11/60 computer, and for all subsequent computations, the Enraf-Nonius SDP/V18 [36] package was used, with the exception of a local data-reduction program. Three standard reflections measured every hour during the entire data-collection period showed a mean loss of 8% in intensity which was corrected using a time-dependent linear interpolation function.

The raw step-scan data were converted to intensities using the Lehman–Larsen [37] method and then corrected for Lorentz, polarisation and absorption factors (transmission factors between 0.09 and 0.16). A single data set of 2559 reflections having $I > 3\sigma(I)$ was used for determining and refining the structure.

The structure was solved using the heavy atom method. After refinement of the heavy atoms, a difference-Fourier map revealed maxima of residual electronic density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H 0.95 Å) and isotropic temperature factors of 5 Å^2 but not refined. Full least-squares refinement converged to $R(F) = 0.040$ and $R_\omega(F) = 0.06$ ($\omega = 1/(\sigma^2_{count} + (pI)^2)$. The unit-weight observation was 1.39 for $p = 0.08$. A final difference map revealed no significant maxima (0.15 eÅ^{-3}).

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