Theoretical Studies of Molybdenum Peroxo Complexes [$MoO_n(O_2)_{3-n}(OPH_3)$] as Catalysts for Olefin Epoxidation†

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The equilibrium geometries of the molybdenum oxo/peroxo compounds $MoO_n(O_2)_{3-n}$ and the related complexes [$MoO_n(O_2)_{3-n}(OPH_3)$] and [$MoO_n(O_2)_{3-n}(OPH_3)(H_2O)$] ($n = 0-3$) have been calculated using gradient-corrected density-functional theory at the B3LYP level. The structures of the peroxo complexes with ethylene ligands [$MoO_n(O_2)_{3-n}(C_2H_4)$] and [$MoO_n(O_2)_{3-n}(OPH_3)(C_2H_4)$] ($n = 1, 2$) where ethylene is directly bonded to the metal have also been optimized. Calculations of the metal−ligand bond-dissociation energies show that the OPH_3 ligand in [$MoO_n(O_2)_{3-n}(OPH_3)$] is much more strongly bound than the ethylene ligand in [$MoO_n(O_2)_{3-n}(C_2H_4)$]. This makes the substitution of phosphane oxide by olefins in the epoxidation reaction unlikely. An energy-minimum structure is found for [$MoO(O_2)_2(OPH_3)(C_2H_4)$], for which the dissociation of C_2H_4 is exothermic with $D_0 = -5.2$ kcal/mol. The reaction energies for the perhydrolysis of the oxo complexes with H_2O_2 and the epoxidation of ethylene by the peroxo complexes have also been calculated. The peculiar stability of the diperoxo complex [$MoO(O_2)_2(OPH_3)(H_2O)$] can be explained with the reaction energies for the perhydrolysis of [$MoO_n(O_2)_{3-n}(OPH_3)(H_2O)$]. The first perhydrolysis step yielding the monoperoxo complex is less exothermic than the second perhydrolysis reaction, but the further reaction with H_2O_2 yielding the unknown triperoxo complex is clearly endothermic. CDA analysis of the metal−ethylene bond shows that the binding interactions are mainly caused by charge donation from the ligand to the metal.

Introduction

Approximately half of the 4 million tons of propylene oxide produced anually is still made via a chlorohydrin intermediate, despite the high cost and the environmental impact of this technique.[1] Because the replacement of the chlorohydrin process is a holy grail for the chemical industry, enormous research efforts focus on the development of new epoxidation methods.[2] The common route of ethylene epoxidation on silver surfaces is not applicable to alkyl-substituted olefins due to the more favorable oxidation of the allylic C−H bonds.[3] More convenient to solve this chemoselectivity problem than heterogeneous catalysis is the employment of transition-metal complexes for homogeneous catalysis. Since the development of the Halcon-Arco process,[4] diperoxo complexes of groups 5,[5] 6,[6,7] and 7[8] have moved into the center of chemical research. A successful strategy has recently been patented by BASF:[9] Molybdenum diperoxo complexes [$MoO(O_2)_2LL'$] (e.g., L = OPR_3, R = *n*-dodecyl, L′ = H_2O) derived from Mimoun's pioneering work[10] (L = hmpa, L′ = H_2O) were tuned toward their use as catalysts in a biphasic system.[11] The perhydrolysis[12] of the molybdenum trioxide compound occurs in the hydrogen peroxide/water phase. During phase transfer into the chloroform/olefin phase, the diperoxo complex is transformed into the catalytically active species [$MoO(O_2)_2(OPR_3)$],[13] from which an oxygen is transferred to the olefin in the rate-determining step of the catalytic process.[11]

Despite the large commercial interest, the peculiar role of the active catalyst is still poorly understood. The questions

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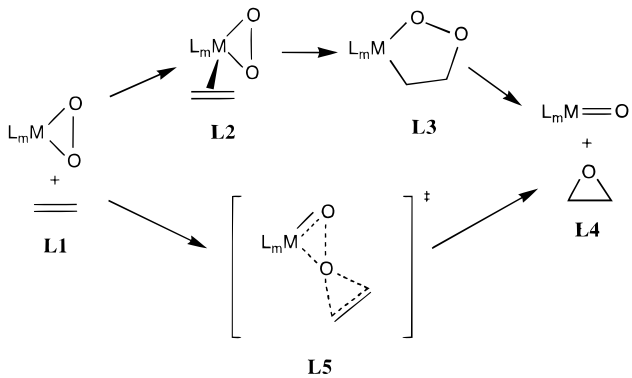
Scheme 1. Reaction Pathways of Olefin Epoxidation with $[MoO(O_2)_2L_m]$ Suggested by Mimoun (Upper Way via **L2** and **L3**) and by Sharpless (via Transition State **L5**)



involved are of a general interest, and they concern the properties of all peroxo compounds catalyzing olefin epoxidation. One issue is about the fact that the active molybdenum catalyst has two peroxo groups although the perhydrolysis of the molybdenum trioxide compounds $[MoO_3L_m]$ could in principle yield three different peroxides $[MoO_n(O_2)_{3-n}L_m]$ with $n = 0-2$. It seems that the diperoxide ($n = 1$) is particularly stable: Several X-ray structure analyses of complexes with the formula $[MoO(O_2)_2LL']$ were reported, but there is no experimental structure known to us for analogous monoperoxo or triperoxo complexes.[14] The question about the peculiar role of the complexes with the formula $[MoO(O_2)_2L_m]$ with the ligands OPH_3 and H_2O in the context of olefin epoxidation is addressed in this paper.

A second topic of our work concerns the possibilities of olefin coordination to the metal in the compounds $[MoO_n(O_2)_{3-n}(C_2H_4)]$ and $[MoO_n(O_2)_{3-n}(OPH_3)(C_2H_4)]$ ($n = 1, 2$). According to the Dewar−Chatt−Duncanson (DCD)[15] model, there is no back-donation from d^0 metal centers to the olefin, which is generally considered as an important if not dominant part of the binding interactions. Gisdakis et al. did not find an energy minimum structure for ethylene complexes of analogous methyltrioxorhenium(VII) (MTO) compounds.[16] However, olefin coordination to the metal is frequently discussed as the initial step of olefin epoxidation: Two publications[17,18] about the stoichiometric olefin epoxidation by $[MoO(O_2)_2(hmpa)]$ actuated a long controversy, which is still lasting (Scheme 1).[19] In 1970, Mimoun et al. interpreted their results of kinetic investigations in terms of a multiple-step mechanism.[17] They suggested a coordination of the olefin at the metal (**L2**) and a subsequent cycloinsertion into a Mo−peroxo bond. The metalla-2,3-dioxolane[20] **L3** decomposes to the epoxide and the monoperoxo complex **L4**.[17] In contrast, Sharpless et al. postulated two years later a concerted mechanism via a transition state **L5** involving the carbon atoms and the transferred oxygen.[18] Concerning the olefin-coordinated species **L2**, a distinction between a *substitution* of the phosphane oxide by the olefin and an olefin *addition* was not always pointed out, which led to some confusion in the literature. Mimoun favors substitution[21] whereas Arakawa et al. repute the addition as more likely.[22] Although additional experimental[23] and theoretical[24] studies have been performed, the controversy has not been settled yet. Recently, the reaction mechanisms of olefin epoxidation catalyzed by $[MoO(O_2)_2(L\text{-}L')]$ (L-L′ = 3-pyrazolyl-pyridine-*N*,*N*′ type ligands)[25] and by MTO[16,26] in the presence of *t*-butyl-OOH and H_2O_2, respectively, have been illuminated. However, these processes differ significantly from the $[MoO(O_2)_2(OPR_3)]$ system,[9,10] and the results might not be transferable. Therefore, we addressed the question about the stability of complexes with the formulas $[MoO_n(O_2)_{3-n}(C_2H_4)]$ and $[MoO_n(O_2)_{3-n}(OPH_3)(C_2H_4)]$ ($n = 1, 2$) in our study.

Methods

The geometries of the molecules were optimized using the 3-parameter fit of the exchange potentials introduced by Becke (B3LYP).[27] Relativistic small-core ECPs[28] with a valence-basis-set splitting (441/2111/31) were used for Mo, while 6-31G(d) all-electron basis sets were employed for the other atoms.[29] This is our standard basis set II.[30] Vibrational frequencies and zero-point energy contributions (ZPE) were also calculated at B3LYP/II. All structures reported here are minima (NIMAG = 0) on the potential energy surface. The ZPE corrections are unscaled. Improved total energies were calculated at the B3LYP level using the same ECP and valence basis set for Mo, but totally uncontracted and augmented with one set of f-type polarization functions ($\zeta = 1.04$),[31] together with 6-31+G(d) basis sets at the other atoms.[32] This basis set combination is denoted III+.[33]

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Unless otherwise mentioned, all energies reported refer to the B3LYP/III+//B3LYP/II level of theory. The calculations were carried out with the program packages Gaussian 94[34] and 98.[35]

The donor−acceptor interactions in the olefin complexes were examined using the charge-decomposition analysis (CDA),[36] which is a quantitative interpretation of the DCD model. The Kohn−Sham orbitals of the olefin complexes are expressed as a linear combination of the orbitals of ethylene and the remaining metal fragment [M] in the geometry of the complex. The orbital contributions are divided into the mixing of the occupied MOs of ethylene and the vacant orbitals of [M] (donation $C_2H_4 \rightarrow$[M]), the mixing of the vacant MOs of ethylene and the occupied orbitals of [M] (back-donation $C_2H_4 \leftarrow$[M]), and the mixing of the occupied MOs of ethylene and the occupied orbitals of [M] (repulsive polarization $C_2H_4 \leftrightarrow$[M]). A fourth term denoted as residue term Δ gives the mixing of the unoccupied MOs of ethylene and the unoccupied MOs of [M]. The Δ term should be approximately zero if a discussion of the olefin complexes in terms of donor−acceptor interactions is permissible. The CDA calculations were performed using the program CDA 2.1.[37]

Geometries and Bond Dissociation Energies

Figure 1 shows the theoretically predicted geometries of the compounds $MoO_n(O_2)_{3-n}$ (**1**−**4**), [$MoO_n(O_2)_{3-n}(OPH_3)$] (**5**−**8**), [$MoO_n(O_2)_{3-n}(OPH_3)(H_2O)$] (**9**−**12**) with $n = 0-3$ and [$MoO_n(O_2)_{3-n}(C_2H_4)$] (**13**, **14**) and [$MoO_n(O_2)_{3-n}(OPH_3)(C_2H_4)$] (**15**) with $n = 1$, 2 which have been located as energy minima on the potential energy surfaces. Table 1 gives the calculated energies. Table 2 lists the bond dissociation energies (BDEs) of the ligands OPH_3, H_2O, and C_2H_4, respectively.

The calculations predict that MoO_3 is not planar but has a pyramidal equilibrium geometry with C_{3v} symmetry. This is an interesting result, because the question whether molybdenum trioxide is planar or pyramidal has not definitely been answered yet.[38] The vibrational frequencies of MoO_3 were interpreted in favor of a pyramidal C_{3v} symmetry.[39] The interpretation of the vibrational spectrum was later questioned, however.[40] Geometry optimization of planar MoO_3 with enforced D_{3h} symmetry led to a structure which is a transition state that is 7.2 kcal/mol (B3LYP/III+ including ZPE) higher in energy than the C_{3v} form.

The calculations show that the Mo═O double bond becomes clearly shorter upon peroxdiation of the metal from the gas phase structure of MoO_3 (**1**) (1.727 Å) to **2** (1.712 Å) to **3** (1.690 Å, Figure 1). The O−O distances of the peroxo complexes do not exhibit a regular trend when the number of peroxo ligands increases. It is interesting to note that the O−O bond length of the metal diperoxide $MoO(O_2)_2$ (**3**) is clearly *shorter* than in H_2O_2, while the monoperoxide **2** has a longer O−O bond than in hydrogen peroxide. The O−O distance in the triperoxo compound **4** is nearly the same as in H_2O_2. We want to point out that the peroxo ligands in **3** and particularly **4** have two significantly different Mo−O distances. The diperoxo compound has C_s symmetry. A C_{2v}-symmetric structure with symmetrical peroxo ligands, which is not a minimum on the potential energy surface, was calculated at B3LYP/II to be 18.0 kcal/mol higher in energy than **3**.

Figure 1 shows that the geometries of the $MoO_n(O_2)_{3-n}$ moieties in [$MoO_n(O_2)_{3-n}(OPH_3)$] (**5**−**8**) are only slightly disturbed by the presence of the OPH_3 ligand, compared with **1**−**4**. The binding of the phosphane oxide ligand to **1**−**4** yields mostly longer metal−oxygen bond lengths in the complexes **5**−**8**. Noteworthy is the significant anomeric effect[41] in **5** and **8**. The σ-type electron lone pair of the oxygen atom of the OPH_3 ligand interacts via negative hyperconjugation[42] with the anti-bonding σ^* and π^* orbitals of the Mo−O moieties situated anti to the lone pair. This is schematically shown in Figure 2. The hyperconjugative interactions lead to a longer Mo−O3 bond in **5** and longer Mo−O5/6 bonds in **8** (Figure 1). Stereoelectronic effects due to negative hyperconjugation are well-known in organic chemistry.[41] The more common name in transition-metal chemistry is agostic interactions, which basically refers to the same electronic interactions.

The Mo−OPH_3 bond energies of **5**−**8** are rather high (Table 2). The bond energies become lower when the number of peroxo groups increases from zero ($D_0 = 51.1$ kcal/mol) to one ($D_0 =$ 42.5 kcal/mol), two ($D_0 = 36.7$ kcal/mol), and three ($D_0 = 34.2$ kcal/mol). This means that the Lewis acidity of the molybdenum oxides/peroxides has the order **1** ≫ **2** > **3** > **4**. The binding energies of an additional water ligand in the complexes [$MoO_n(O_2)_{3-n}(OPH_3)(H_2O)$] (**9**−**12**) are much smaller, only 5.8−10.8 kcal/mol (Table 2). Two isomers were found for each complex. Three complexes have isomers with a cis arrangement of H_2O and OPH_3 (**9a**, **10a**, **12a**) and with a trans arrangement (**9b**, **10b**, **12b**). The complex **11** has two forms, **11a** and **11b**; both of them have H_2O and OPH_3 in a cis arrangement. In **11a** the water ligand is trans to Mo═O, while in **11b** the OPH_3 ligand is trans to Mo═O. It is interesting to note that the cis form **9a** is more stable than **9b**, while the trans forms **10b** and **12b** are lower in energy than the cis isomers **10a** and **12a** (Table 1). The energy differences between the isomeric forms of **9**−**12** are not very high, between 1.0 kcal/mol for **12** and 5.3 kcal/mol for **11**.

The theoretical prediction that **11a** is more stable than **11b** is in agreement with an X-ray structure analysis of [$MoO(O_2)_2$-($OP(NMe_2)_3)(H_2O)$], which has a cis arrangement of the water and phosphane oxide ligands and the H_2O ligand trans to Mo═

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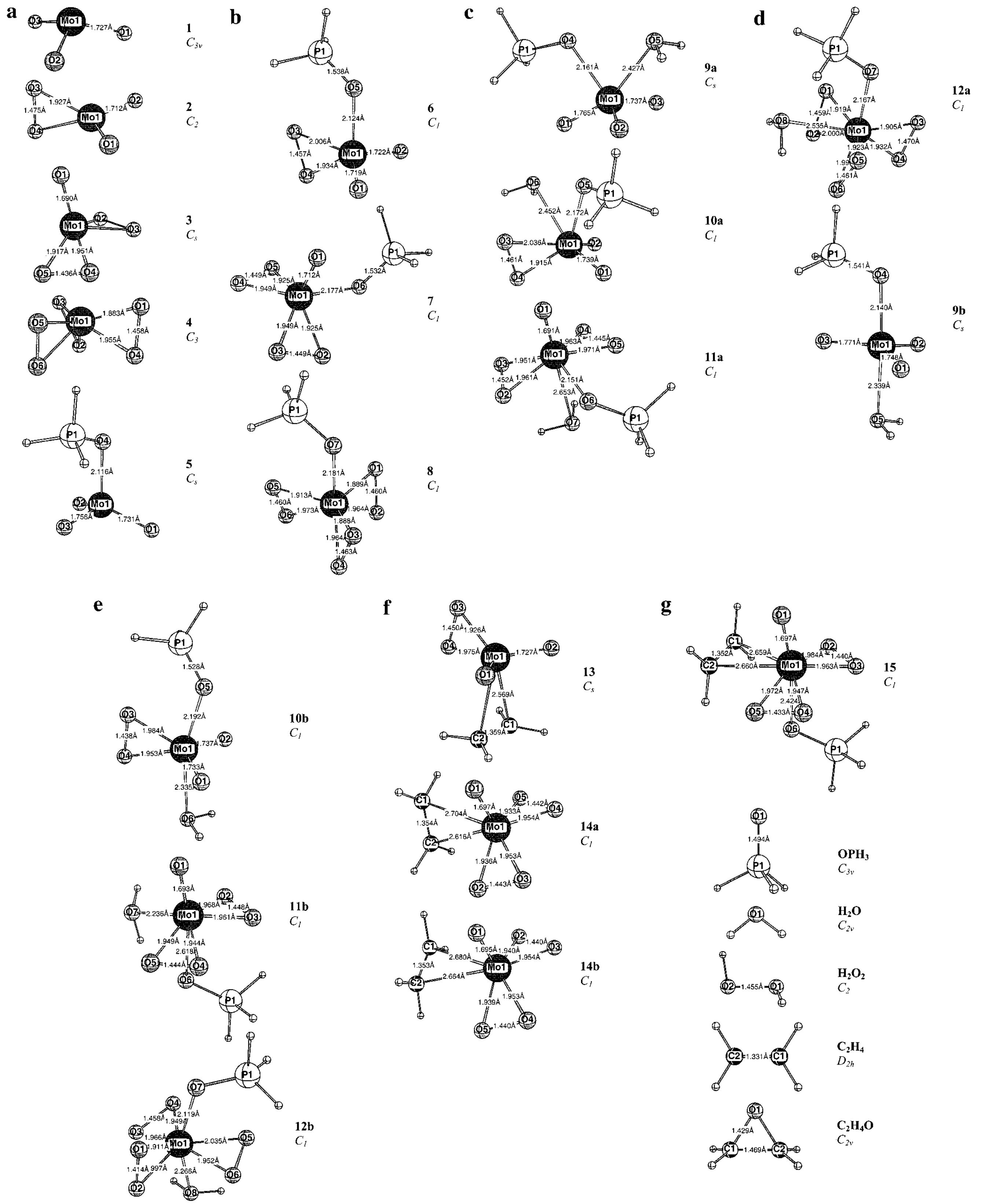

Figure 1. Optimized geometries (B3LYP/II) of the molecules.

O.[43] Figure 3 shows a comparison of the calculated geometries at B3LYP using basis sets II and III+ with the experimental values. The agreement between theory and experiment is satisfactory with two exceptions. One exception is the Mo−OH_2 distance, which is calculated being much too long. The discrepancy between the calculated and the experimental results is at least partly due to solid-state effects. It has been shown that donor−acceptor bonds are always longer in the gas phase than in the solid state, and that the bond shortening with respect to the free molecule increases when the bond becomes weaker.[44]

(43) Le Carpentier, J.-M.; Schlupp, R.; Weiss, R. *Acta Crystallogr.* **1972**, *B28*, 1278.

Table 1. Calculated Total Energies E_{tot}(II) (B3LYP/II) and E_{tot}(III+) (B3LYP/III+//B3LYP/II) (Au), Relative Energies E_{rel}(III+) (kcal/mol), Zero-point Energies ZPE (B3LYP/II) (kcal/mol), and Number *i* of Imaginary Frequencies of the Optimized Structures

structure	no.	sym.	E_{tot}(II)	E_{tot}(III+)	E_{rel}(III+)	ZPE	*i*
MoO_3	**1**	C_{3v}	−293.215 68	−293.257 03		5.5	0
$MoO_2(O_2)$	**2**	C_{2v}	−368.372 61	−368.416 51		7.1	0
$MoO(O_2)_2$	**3**	C_s	−443.526 28	−443.568 33		9.5	0
$Mo(O_2)_3$	**4**	C_3	−518.634 64	−518.678 81		10.9	0
$[MoO_3(OPH_3)]$	**5**	C_s	−711.655 45	−711.704 90		26.9	0
$[MoO_2(O_2)(OPH_3)]$	**6**	C_1	−786.801 63	−786.851 12		28.8	0
$[MoO(O_2)_2(OPH_3)]$	**7**	C_1	−861.943 79	−861.992 94		30.8	0
$[Mo(O_2)_3(OPH_3)]$	**8**	C_1	−937.049 62	−937.099 72		32.3	0
$[MoO_3(OPH_3)(H_2O)]$	**9a**	C_s	−788.091 82	−788.147 30	0.0	42.9	0
$[MoO_3(OPH_3)(H_2O)]$	**9b**	C_s	−788.086 01	−788.141 39	3.7	42.8	0
$[MoO_2(O_2)(OPH_3)(H_2O)]$	**10a**	C_1	−863.226 46	−863.282 24	0.0	44.7	0
$[MoO_2(O_2)(OPH_3)(H_2O)]$	**10b**	C_1	−863.233 67	−863.289 01	−4.2	45.0	0
$[MoO(O_2)_2(OPH_3)(H_2O)]$	**11a**	C_1	−938.380 47	−938.436 13	0.0	47.0	0
$[MoO(O_2)_2(OPH_3)(H_2O)]$	**11b**	C_1	−938.371 92	−938.427 61	5.3	46.9	0
$[Mo(O_2)_3(OPH_3)(H_2O)]$	**12a**	C_1	−1013.479 31	−1013.534 38	0.0	48.7	0
$[Mo(O_2)_3(OPH_3)(H_2O)]$	**12b**	C_1	−1013.482 91	−1013.535 97	−1.0	49.2	0
$[MoO_2(O_2)(C_2H_4)]$	**13**	C_s	−447.004 50	−447.049 00		41.6	0
$[MoO(O_2)_2(C_2H_4)]$	**14a**	C_1	−522.147 30	−522.191 57	0.0	43.6	0
$[MoO(O_2)_2(C_2H_4)]$	**14b**	C_1	−522.146 68	−522.190 53	0.7	43.6	0
$[MoO(O_2)_2(OPH_3)(C_2H_4)]$	**15**	C_1	−940.528 22	−940.579 15		64.7	0
OPH_3		C_{3v}	−418.353 67	−418.363 50		19.6	0
H_2O		C_{2v}	−76.407 02	−76.421 14		13.3	0
H_2O_2		C_2	−151.529 76	−151.545 15		16.5	0
C_2H_4		D_{2h}	−78.585 82	−78.591 65		32.1	0
C_2H_4O		C_{2v}	−153.783 33	−153.792 81		36.2	0

Table 2. Calculated Stabilization Energies (B3LYP/III+//B3LYP/II) (kcal/mol)[a]

reaction	energy
MoO_3 (**1**) + OPH_3 → $[MoO_3(OPH_3)]$ (**5**)	−53.0 (−51.1)
$MoO_2(O_2)$ (**2**) + OPH_3 → $[MoO_2(O_2)(OPH_3)]$ (**6**)	−44.6 (−42.5)
$MoO(O_2)_2$ (**3**) + OPH_3 → $[MoO(O_2)_2(OPH_3)]$ (**7**)	−38.3 (−36.7)
$Mo(O_2)_3$ (**4**) + OPH_3 → $[MoO(O_2)_2(OPH_3)]$ (**8**)	−36.0 (−34.2)
$[MoO_3(OPH_3)]$ (**5**) + H_2O → $[MoO_3(OPH_3)(H_2O)]$ (**9a**)	−13.3 (−10.6)
$[MoO_2(O_2)(OPH_3)]$ (**6**) + H_2O → $[MoO_2(O_2)(OPH_3)(H_2O)]$ (**10b**)	−10.5 (−7.6)
$[MoO(O_2)_2(OPH_3)]$ (**7**) + H_2O → $[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11a**)	−13.8 (−10.8)
$[Mo(O_2)_3(OPH_3)]$ (**8**) + H_2O → $[Mo(O_2)_3(OPH_3)(H_2O)]$ (**12b**)	−9.5 (−5.8)
$MoO_2(O_2)$ (**2**) + C_2H_4 → $[MoO_2(O_2)(C_2H_4)]$ (**13**)	−25.6 (−23.3)
$MoO(O_2)_2$ (**3**) + C_2H_4 → $[MoO(O_2)_2(C_2H_4)]$ (**14a**)	−19.8 (−17.9)
$[MoO_2(O_2)(OPH_3)]$ (**6**) + C_2H_4 → $[MoO_2(O_2)(C_2H_4)]$ (**13**) + OPH_3	19.0 (19.2)
$[MoO(O_2)_2(OPH_3)]$ (**7**) + C_2H_4 → $[MoO(O_2)_2(C_2H_4)]$ (**14a**) + OPH_3	18.5 (18.8)
$[MoO(O_2)_2(OPH_3)]$ (**7**) + C_2H_4 → $[MoO(O_2)_2(OPH_3)(C_2H_4)]$ (**15**)	3.4 (5.2)

[a] ZPE-corrected (B3LYP/II) values are given in parentheses.

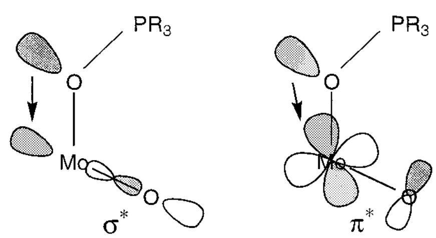

Figure 2. Schematic representation of the negative hyperconjugation (anomeric effect, agostic interactions) between the *σ*-type lone-pair electrons of the oxygen atoms of the OPH_3 group and a Mo−X *σ** bond and a Mo−X *π** bond, respectively, situated *anti* to the lone pair.

Table 2 shows that the Mo−OH_2 bond of **11a** is not very strong (D_0 = 10.8 kcal/mol) and, thus, it should become significantly shorter in the solid state. The second major difference between theory and experiment concerns the bond angle Mo−O−P. The calculations predict bond angles of 123.6° and 126.2°at the two levels of theory, while the Mo−O−P geometry in the crystal structure is approximately linear (173.9°).[43] This arrangement might be caused by the electronic effect of the amido groups in the $OP(NMe_2)$ ligand and by the steric repulsion of the more bulky NMe_2 substituent. Note that the agreement between theory and experiment becomes better for some bond angles when the basis set is improved from II to III+, while for others it is not the case.

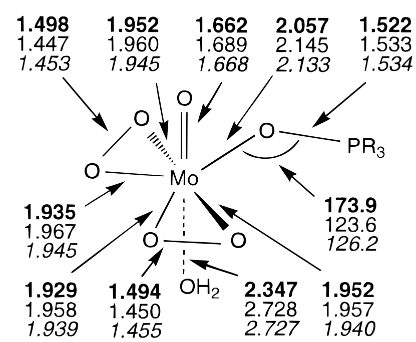

Figure 3. Comparison of the experimental and calculated geometry of $[MoO(O_2)_2(OPR_3)(H_2O)]$. Experimental values (boldface R = $N(CH_3)_2$) are taken from Le Carpentier et al.: Le Carpentier, J.-M.; Schlupp, R.; Weiss, R. *Acta Crystallogr* **1972**, *B28*, 1278. The calculated values (R = H, **11a**) have been obtained at B3LYP/II (plain) and at B3LYP/III+ (italic).

Geometry optimizations have been carried out for energy-minimum structures of the peroxo complexes $[MoO_n(O_2)_{3-n}(C_2H_4)]$

(44) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

Table 3. Calculated Perhydrolysis Energies and Peroxide-Exchange Energies (B3LYP/III+//B3LYP/II) (kcal/mol)[a]

reaction	energy
MoO_3 (**1**) + H_2O_2 → $MoO_2(O_2)$ (**2**) + H_2O	−22.3 (−23.9)
$MoO_2(O_2)$ (**2**) + H_2O_2 → $MoO(O_2)_2$ (**3**) + H_2O	−17.4 (−18.2)
$MoO(O_2)_2$ (**3**) + H_2O_2 → $Mo(O_2)_3$ (**4**) + H_2O	8.5 (6.6)
$[MoO_3(OPH_3)$ (**5**) + H_2O_2 → $[MoO_2(O_2)(OPH_3)]$ (**6**) + H_2O	−13.9 (−15.2)
$[MoO_2(O_2)(OPH_3)]$ (**6**) + H_2O_2 → $[MoO(O_2)_2(OPH_3)]$ (**7**) + H_2O	−11.2 (−12.4)
$[MoO(O_2)_2(OPH_3)]$ (**7**) + H_2O_2 → $[MoO(O_2)_2(OPH_3)]$ (**8**) + H_2O	10.8 (9.1)
$[MoO_3(OPH_3)(H_2O)]$ (**9a**) + H_2O_2 → $[MoO_2(O_2)(OPH_3)(H_2O)]$ (**10b**) + H_2O	−11.1 (−12.2)
$[MoO_2(O_2)(OPH_3)(H_2O)]$ (**10b**) + H_2O_2 → $[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11a**) + H_2O	−14.5 (−15.6)
$[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11a**) + H_2O_2 → $[MoO(O_2)_2(OPH_3)(H_2O)]$ (**12b**) + H_2O	15.2 (14.1)
2 + **2** → **1** + **3**	4.8 (5.7)
6 + **6** → **5** + **7**	2.8 (2.8)
10b +**10b** → **9a** + **11a**	−3.4 (−3.3)

[a] ZPE-corrected values (B3LYP/II) are given in parentheses.

(n = 1, 2) where ethylene is directly bonded to the metal atom.[45] Three structures **13**, **14a**, and **14b** were found. Figure 1 shows the geometries of $[MoO_2(O_2)(C_2H_4)]$ (**13**) and the energetically nearly degenerate isomers of $[MoO(O_2)_2(C_2H_4)]$ (**14a** and **14b**), where the ethylene ligand has two different orientations with respect to the oxygen atoms. This result qualitatively deviates from an exploration of the potential energy surface of **14** at the extended-Hückel level.[24b] The bond energies of ethylene in **13**−**14b** are only ~$^1/_2$ of the BDEs of OPH_3 in the corresponding complexes **6** and **7** (Table 2). Thus, a *substitution* of the phosphane oxide ligand of **6** and **7** by ethylene is a highly endothermic process. The binding of ethylene to molybdenum yields only small changes in the geometries of the $MoO_n(O_2)_{3-n}$ moieties compared with **2** and **3**.

We also searched for peroxo complexes $[MoO_n(O_2)_{3-n}(C_2H_4)(OPH_3)]$ (n = 1, 2) where the ligands ethylene and phosphane oxide both are bound to molybdenum. While a complex $[ReO(O_2)_2(C_2H_4)(Me)]$ does not exist,[16] the analogous molybdenum complex $[MoO(O_2)_2(C_2H_4)(OPH_3)]$ (**15**) was found as an energy minimum. However, attempts to optimize the corresponding monoperoxo complex $[MoO_2(O_2)(C_2H_4)(OPH_3)]$ failed. The molecule **15** can be considered as a trigonal-bipyramidal complex where the peroxo ligands and ethylene are in the equatorial positions while the oxo group and the OPH_3 ligand are in the axial positions. Note that the compound $[MoO(O_2)_2(OPH_3)]$ (**7**) has the oxo group and the OPH_3 ligand cis to each other (Figure 1). The isomer of $[MoO(O_2)_2(OPH_3)]$ with a trans arrangement of these ligands is not a minimum on the potential energy surface. For **15**, the BDE of the C_2H_4 is exothermic by D_0 = −5.2 kcal/mol (Table 2). Although **15** is unstable with regard to loss of the ethylene ligand, an *addition* of the olefin as the initial step of epoxidation remains possible in principle, unlike for the MTO system, for which this reaction step has recently been ruled out.[16]

Energies of the Perhydrolysis and Epoxidation Reactions

To obtain information about the peculiar stability of the diperoxides, we calculated the reaction energies for perhydrolysis of the molybdenum oxides with and without further ligands by H_2O_2 yielding the respective peroxides. The results are given in Table 3. Perhydrolysis of MoO_3 (**1**) yielding the monoperoxide $MoO_2(O_2)$ (**2**) is strongly exothermic with D_0 = −23.9 kcal/mol. The next perhydrolysis step yielding the diperoxide $MoO(O_2)_2$ (**3**) is less exothermic but still energetically favorable with D_0 = −18.2 kcal/mol. However, the formation of the triperoxide $Mo(O_2)_3$ (**4**) by further perhydrolysis of **3** is thermodynamically disfavored, because the reaction is endothermic with D_0 = +6.6 kcal/mol.

The reaction of the phosphane oxide complexes $[MoO_n(O_2)_{3-n}(OPH_3)]$ with H_2O_2 has a somewhat different energy profile than the perhydrolyses of $MoO_n(O_2)_{3-n}$. Table 3 shows that the perhydrolysis of the trioxide $[MoO_3(OPH_3)]$ (**5**) and the dioxide $[MoO_2(O_2)(OPH_3)]$ (**6**) are again both exothermic. The OPH_3 ligand makes the perhydrolysis of the trioxide much less exothermic (D_0 = −15.2 kcal/mol) compared with free MoO_3. The phosphane oxide ligand reduces also the exothermicity of the reaction of the dioxide **6** with H_2O_2 (D_0 = −12.4 kcal/mol) with regard to free $MoO_2(O_2)$ but to a lesser extent. Perhydrolysis of **7** yielding the triperoxide $[Mo(O_2)_3(OPH_3)]$ (**8**) remains endothermic with D_0 = +9.1 kcal/mol.

The calculated reaction energies for the reaction of the complexes $[MoO_n(O_2)_{3-n}(OPH_3)(H_2O)]$ (**9**−**11**) with H_2O_2 yielding the compounds **10**−**12** as reaction products give an explanation for the experimental result that only substituted analogues of the diperoxide **11** could be isolated so far. Table 3 shows that the perhydrolyses of the trioxide **9** and the dioxide **10** are still exothermic, having reaction energies similar to those of the perhydrolyses of **5** and **6**, respectively. However, the reaction of **10** with H_2O_2 yielding the diperoxide $[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11**) is now predicted to be more exothermic (D_0 = −15.6 kcal/mol) than perhydrolysis of **9** (D_0 = −12.2 kcal/mol). Further perhydrolysis of **11** yielding the triperoxide **12** is clearly endothermic with D_0 = 14.1 kcal/mol. This means that the thermodynamically favored perhydrolysis reaction of the molybdenum oxide in the presence of water and phosphane-oxide ligands is the diperoxide **11**. Table 3 shows that the "dismutation" reaction of the dioxide **10** yielding the trioxide **9** and the diperoxide **11** is exothermic with D_0 = −3.3 kcal/mol, while the respective dismutation reactions of **2** and **6** are endothermic. The calculated reaction energies reveal that the molybdenum diperoxo complex **11** is thermodynamically favored over the compounds **9**, **10**, and **12**.

We also calculated the reaction energies for the epoxidation of ethylene by the different peroxide complexes (Table 4). The results directly follow from the energies of the perhydrolysis reactions (Table 3) and the energy of ethylene epoxidation by H_2O_2. The calculations predict that the epoxidation of ethylene with $MoO_n(O_2)_{3-n}$ (**2**−**4**) is always exothermic, and that the exothermicity increases with the trend $n = 2 < 1 < 0$. This

(45) We calculated also the geometry of the complex where ethylene is bonded to molybdenum trioxide. The complex $[MoO_3(C_2H_4)]$ is a minimum on the potential energy surface and has a rather strong Mo−C_2H_4 bond (D_0 = −37.9 kcal/mol). This is an interesting result because OsO_4 does not form a complex with an Os−C_2H_4 bond (Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 4937). Since $[MoO_3(C_2H_4)]$ does not play a role in the epoxidation reaction, we do not discuss the results in this paper. We are presently investigating the structures and stabilities of transition metal oxide complexes with ethylene ligands.

Table 4. Calculated Epoxidation Energies (B3LYP/III+//B3LYP/II) (kcal/mol)[a]

reaction	energy
$MoO_2(O_2)$ (**2**) + C_2H_4 → MoO_3 (**1**) + C_2H_4O	−26.7 (−23.7)
$MoO(O_2)_2$ (**3**) + C_2H_4 → $MoO_2(O_2)$ (**2**) + C_2H_4O	−31.0 (−29.4)
$Mo(O_2)_3$ (**4**) + C_2H_4 → $MoO(O_2)_2$ (**3**) + C_2H_4O	−56.9 (−54.2)
$[MoO_2(O_2)(OPH_3)]$ (**6**) + C_2H_4 → $[MoO_3(OPH_3)]$ (**5**) + C_2H_4O	−34.5 (−32.4)
$[MoO(O_2)_2(OPH_3)]$ (**7**) + C_2H_4 → $[MoO_2(O_2)(OPH_3)]$ (**6**) + C_2H_4O	−37.2 (−35.2)
$[Mo(O_2)_3(OPH_3)]$ (**8**) + C_2H_4 → $[MoO(O_2)_2(OPH_3)]$ (**7**) + C_2H_4O	−59.2 (−56.7)
$[MoO_2(O_2)(OPH_3)(H_2O)]$ (**10b**) + C_2H_4 → $[MoO_3(OPH_3)(H_2O)]$ (**9a**) + C_2H_4O	−37.3 (−35.4)
$[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11a**) + C_2H_4 → $[MoO_2(O_2)(OPH_3)(H_2O)]$ (**10b**) + C_2H_4O	−33.9 (−32.0)
$[Mo(O_2)_3(OPH_3)(H_2O)]$ (**12b**) + C_2H_4 → $[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11a**) + C_2H_4O	−63.6 (−61.7)
H_2O_2 + C_2H_4 → H_2O + C_2H_4O	−48.4 (−47.5)

[a] ZPE-corrected (B3LYP/II) values are given in parentheses.

means that the epoxidation becomes thermodynamically more favored when the number of peroxide groups becomes larger. The OPH_3 ligands make the complexes $[MoO_n(O_2)_{3-n}(OPH_3)]$ (**6**−**8**) become stronger epoxidating agents than **2**−**4**, but the trend for *n* remains the same. The results for the water complexes $[MoO_n(O_2)_{3-n}(OPH_3)(H_2O)]$ (**10**−**12**) are quite interesting. Water further enhances the thermodynamic driving force of the epoxidation with the mono- and triperoxides **10** and **12** with respect to **6** and **8**, respectively, while thermodynamically the epoxidation strength of **11** is slightly weaker than that of **7**. The calculations indicate that the reason why the diperoxo complex **11** but not the monoperoxide **10** and triperoxide **12** is utilized as epoxidation agent is the thermodynamic stability of the former complex. Perhydrolysis of molybdenum triperoxo complexes with phosphane oxide and water ligands yields for thermodynamical reasons only the diperoxide species $[MoO(O_2)_2(OPH_3)(H_2O)]$ (**11**). However, it has been shown that the active oxidant of the epoxidation reaction is $[MoO(O_2)_2(OPR_3)]$, which is formed by dissociation of $[MoO(O_2)_2(OPR_3)(H_2O)]$.[11,17] $[MoO_2(O_2)(OPR_3)]$ does not seem to play a role as oxidant, in contrast to the corresponding tungsten monoperoxo complexes.[23c] We are currently studying the mechanism of olefin epoxidation with $[MoO(O_2)_2(OPR_3)]$ in detail.

Metal−Ethylene Bonding in 13−15

The chemical bonds in metal−olefin complexes are usually discussed either in terms of donor−acceptor interactions which consider the π HOMO and π^* LUMO of ethylene as the most important donor and acceptor orbital of the ligand (Dewar−Chatt−Duncanson model)[15] or as metallacyclopropanes. The ethylene complexes **13**−**15** certainly do not belong to the latter class because the Mo−(C_2H_4) BDEs are not very high, and the C−C bond of the ligand is not much longer than in free ethylene (Figure 1). However, donor−acceptor interactions should only be found in the direction C_2H_4→Mo, because the molybdenum atom has the formal oxidation state VI and, thus, there are no lone-pair electrons available for effective Mo→C_2H_4 π-back-donation.

We analyzed the Mo−ethylene bonds in **13**−**15** with charge-decomposition analysis (CDA).[36] The results are shown in Table 5. There is a significant amount of C_2H_4→[Mo] σ-donation from the occupied π MO of ethylene (which has σ symmetry in the complex), while the [Mo]→C_2H_4 π-back-donation is practically nil. The values for the rest term Δ, which gives the mixing of the unoccupied orbitals of ligand and metal fragment, is ∼0. This means that **13**−**15** should be considered as donor−acceptor complexes and not as metallacyclopropanes.[46] The CDA results

(46) (a) Frenking, G.; Pidun, U. *J. Chem. Soc., Dalton Trans.* **1997**, 1653. (b) Pidun, U.; Frenking, G. *J. Organomet. Chem.* **1996**, *525*, 269. (c) Pidun, U.; Frenking, G. *Organometallics* **1995**, *14*, 5325.

Table 5. CDA Results of the Ethylene Complexes: C_2H_4→Metal Fragment ([M]) Donation *d*, C_2H_4←[M] Back-Donation *b*, C_2H_4↔[M] Repulsive Polarization *r*, and Residue Term Δ

molecule	*d* C_2H_4→[M]	*b* C_2H_4←[M]	*d*/*b*	*r* C_2H_4↔[M]	Δ
13	0.358 (0.262)[b]	0.068 (0.043)[c]	5.26	−0.161	−0.017
14a	0.345 (0.214)[b]	0.052 (0.019)[c]	6.63	−0.164	−0.014
14b	0.345 (0.207)[b]	0.049 (0.027)[d]	7.04	−0.164	−0.013
15	0.341 (0.160)[b]	0.061 (0.024)[e]	5.59	−0.179	−0.017

[a] Main contributions are given in parentheses. [b] HOMO→LUMO. [c] LUMO←HOMO-6. [d] LUMO←HOMO-3. [e] LUMO←HOMO-5.

show that the Mo−C_2H_4 bonding is only caused by ligand → metal σ donation without significant π back-donation.

Summary

The results of this investigation can be summarized as follows.

1. The molybdenum oxides/peroxides $MoO_n(O_2)_{3-n}$ have rather strong bonds with OPH_3 in the complexes $[MoO_n(O_2)_{3-n}(OPH_3)]$. The monoperoxide $MoO_2(O_2)$ and the diperoxide $MoO(O_2)_2$ may also bind ethylene directly at the molybdenum atom yielding the complexes $[MoO_2(O_2)(C_2H_4)]$ and $[MoO(O_2)_2(C_2H_4)]$, respectively. The Mo−C_2H_4 bonds in the latter complexes are significantly weaker than the Mo−OPH_3 bonds in the former species. The diperoxo complex $[MoO(O_2)_2(OPH_3)]$ is also able to bind ethylene, in contrast to the monoperoxo complex $[MoO_2(O_2)(OPH_3)]$ and the corresponding methyltrioxorhenium(VII) compounds.

2. Perhydrolysis of $[MoO_3L_m]$ and $[MoO_2(O_2)L_m]$ with and without ligands L (L = OPH_3 or L = OPH_3 + H_2O) with H_2O_2 yielding the complexes $[MoO_2(O_2)L_m]$ and $[MoO(O_2)_2L_m]$, respectively, are clearly exothermic processes. The formation of the diperoxide is particularly favored in the presence of OPH_3 and H_2O as ligands. The reaction yielding the triperoxide $[Mo(O_2)_3L_m]$ is always endothermic. This explains why diperoxo complexes of molybdenum could become isolated so far, while structures of monoperoxides and triperoxides are not known.

3. The epoxidation of ethylene with $[MoO_n(O_2)_{3-n}L_m]$ (n = 0−2) is a highly exothermic process. The mono- and diperoxo complexes $[MoO_2(O_2)L_m]$ and $[MoO(O_2)_2L_m]$ have a similar thermodynamic driving force for the epoxidation reaction in the presence of ligands.

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