

Quantum chemical study of the mechanisms of oxidation of ethylene by Molybdyl and Tungstyl Chloride

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Abstract. The mechanisms of oxidation of olefins with MoO_2Cl_2 and WO_2Cl_2 are studied with DFT. The formation of epoxide from these reactions is not very feasible by any of the postulated paths. If the epoxide precursor will form at all, it will arise *via* initial $[3+2]_{\text{O,Cl}}$ addition of ethene to MoO_2Cl_2 and WO_2Cl_2 to form an intermediate, followed by re-arrangement to form the precursor, from which the epoxide can be generated by hydrolysis. The chlorohydrin precursor was also found to originate from $[3+2]_{\text{O,Cl}}$ addition of ethene to MO_2Cl_2 . The results also indicate that a dichloride is not a likely product in the oxidation of ethylene by molybdyl chloride. However, in the case of WO_2Cl_2 , the formation of a dichloride may not be precluded. The formation of acetaldehyde and vinyl alcohol from the oxidation of ethylene does not appear energetically feasible with MoO_2Cl_2 , but appears thermodynamically plausible with WO_2Cl_2 . Thus, the oxidation of ethylene with MoO_2Cl_2 will most likely lead to the formation of chlorohydrins predominantly *via* $[3+2]_{\text{O,Cl}}$ addition; oxidation with WO_2Cl_2 may also form chlorohydrins, but only extremely slowly. The oxyhalides MO_2Cl_2 become weaker oxidants in the order $\text{CrO}_2\text{Cl}_2 >> \text{MoO}_2\text{Cl}_2 > \text{WO}_2\text{Cl}_2$. Corresponding to this, reactions involving reduction of the metal $[3+2]$ and $[2+1]$ show a sharp increase in barrier going from Cr to W; reactions without a change in metal oxidation state ($[2+2]$) show much smaller variations, which are possibly mainly determined by sterics.

Keywords. Olefin oxidation; epoxidation; computational; mechanisms

1. Introduction

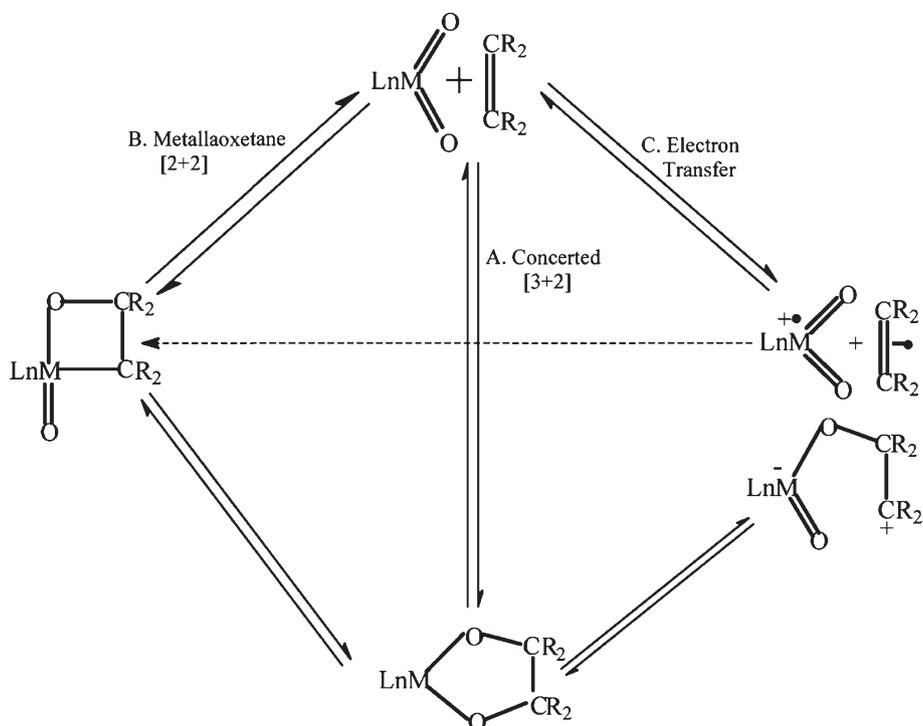
High-valent transition metal oxo compounds, such as osmium tetroxide (OsO_4), chromyl chloride (CrCl_2O_2) and permanganate (MnO_4^-) are known to be very strong oxidizing agents. In their reactions, an oxygen or a halogen is inserted into a C-H linkage or added to an olefinic double bond, a property that has been utilized in a variety of applications ranging from organic synthesis to chemical vapor deposition to catalysis. A major interest is in the selectivity of the oxidation of organic compounds and the specificity of the product(s) formed from these reaction,^{1,2} since oxidations carried out this way is far more specific and relatively gentle compared to oxidations carried out through the direct application of elemental oxygen.

The mechanisms of the oxidation processes have been the subject of a lot of experimental and theoretical studies.^{3–11} For the reaction of osmium tetroxide (OsO_4) with olefins, Criegee *et al.*,^{12,13} proposed a concerted $[3+2]$ cycloaddition pathway (path A

in scheme 1). This proposal was widely accepted by organic chemists^{4,14,15} partly due to the fact that it is analogous with other dipolar cycloadditions. The product of the $[3+2]$ addition, a five-membered metallacycle (osma-2,5-dioxolane), was experimentally characterized, and upon hydrolysis gives diols.⁴

Experimental evidence shows that oxidation of olefins with osmium tetroxide (OsO_4) and permanganate (MnO_4^-) forms predominantly diols without significant epoxide formation. However, oxidation with chromyl chloride (CrCl_2O_2) forms a complex mixture of products with predominantly epoxide formation.^{3,4,16} The main products in the oxidation of alkenes with CrO_2Cl_2 are epoxide, chlorohydrin and in some cases, vicinal dichloride, the formation of which could not be explained by Criegee's concerted pathway. Sharpless *et al.*,³ therefore proposed a mechanism involving organometallic intermediates with chromium-carbon linkages. Particularly, the key feature in the formation of epoxide was postulated to be the involvement of a chromaoxetane, *i.e.*, a four-membered cyclic compound formed *via* a $[2+2]$ interaction between the olefin and an oxo group on the chromium (path B in scheme 1). However,

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Scheme 1. Possible pathways for the reaction of LnMO_2 with Alkene.¹⁸

the work of Tia and Adei⁷ showed that the oxidation of ethylene with Cl_2CrO_2 should form predominantly diols, chlorohydrins and to a less extent, dichlorides without significant epoxide formation.

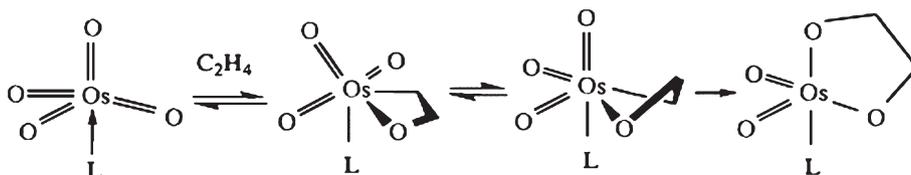
Kochi *et al.*,¹⁷ proposed a third mechanism (path C in scheme 1) to explain the oxidation of olefins by oxo transition metal complexes¹⁷ which involves an initial electron transfer, and addition of the odd electron intermediate to give a metallaioxetane and/or metalladiolate.

Ziegler *et al.*,⁶ studied the [2 + 2] and [2 + 3] cycloaddition mechanisms for the osmium-catalyzed dihydroxylation of olefins using DFT with ammonia and ethylene chosen as models for the base and olefin respectively (scheme 2).

The results from this study indicated that the hypothesis by Sharpless *et al.*,³ a [2 + 2] cycloaddition pathway involving the formation of a four-membered metallacycle as an intermediate should be ruled out because the activation barrier for the [2 + 2] pathway was higher than the activation barrier for the [3 + 2] pathway. Moreover, the addition of an NH_3 ligand to the osmium

catalyst did not reduce the [2 + 2] energy barrier significantly. In contrast, it seemed more feasible that the dihydroxylation reaction proceeds through a [2 + 3] mechanism leading to the formation of a five-membered ring dioxylate intermediate as proposed by Criegee *et al.*,^{12,13} and supported by Corey *et al.*^{14,15} This pathway was found to be exothermic and involved a very small activation barrier of less than 2 kcal/mol.

Rappé *et al.*,¹⁹ studied the mechanism of the reaction of ethylene with chromyl chloride (CrO_2Cl_2) and molybdenyl chloride (MoO_2Cl_2) with the GVB method, focusing on the energies of the intermediates. The results of this study provided support for the [2 + 2] addition pathway to form a metallacyclobutane (metallaioxetane) intermediate, which in turn supports Sharpless's proposal that the organometallic intermediate is likely the common precursor from which all the oxygen-containing products that have been observed arise. Sharpless and Gobel provided additional proof of the stepwise addition pathway by way of non-linear Eyring enantioselectivity-reciprocal of temperature plots for



Scheme 2. Postulated intermediates in the base-free and base-assisted addition of OsO_4 to olefins.

asymmetric dihydroxylations. Computations of the [2 + 2] and [3 + 2] activation barriers for the reactions of OsO₄ with ethylene^{5,6,20} showed that the barriers of the [2 + 2] addition to form the four-membered metallaoxetane ring was very much higher than the barriers for the [3 + 2] addition to form the five-membered osma-2,5-dioxalane, which indicated that the reaction follows the concerted [3 + 2] addition pathway. The work of Houk *et al.*,²¹ also supported the concerted reaction pathway for the addition of OsO₄ with ethylene. For the chromyl chloride (CrO₂Cl₂) system, Ziegler *et al.*,²² performed DFT calculations on the addition of ethene across chromium-oxygen bonds and found the [3 + 2] addition to form the five-membered ring to be more favorable than the [2 + 2] addition to form the four-membered cyclic chromaoxetane. In another study, Ziegler *et al.*,²³ found that contrary to Sharpless' assumption, the formation of the epoxide precursor from the reaction between CrO₂Cl₂ and ethylene does not involve an organometallic intermediate arising from [2 + 2] addition but rather from an ester intermediate formed from the [3 + 2] addition of ethene to the chromium-oxygen bonds in CrO₂Cl₂. A density functional theory study on the oxidation of ethene by ruthenium tetroxide, a well-known active catalyst, by Strassner and Drees,²⁴ proposed that the reaction follows a [3 + 2] addition pathway on the singlet surface, which was found to be 22 kcal/mol lower in activation energy than the [2 + 2] cycloaddition pathway.

In a DFT B3LYP/6-31G* study by Tia and Adei⁷ the activation barrier for the [3 + 2] addition pathway was found to be lower than that for the [2 + 2] pathway, but the dioxylate formed from the [3 + 2] pathway was found to be too stable to be rearranged to the epoxide precursor. It was therefore argued that if an epoxide is formed at all, it must arise from [2 + 2] addition and not by the [3 + 2] addition. The energetics from this study indicates that the reaction of ethylene with Cl₂CrO₂ should form diols predominantly. In another DFT study,⁸ they found that in the reaction of ethylene with osmyl chloride (Os₂Cl₂), the [2 + 2] pathway leading to the formation of metalloxetane was more favoured than the [3 + 2] pathway leading to the dioxylate, whereas for the OsO₄ the [3 + 2] pathway was favored.

It is clear from the literature that there is no agreement on the most preferred pathway for the oxidation of olefins with transition metal oxo-complexes. This work aims at extending the work of Tia and Adei⁷ to include Mo and W, the other members of the group VI metals, so as to draw group trends. We have already shown interesting group trends in the oxidation of olefins with group VII metal oxo complexes.¹⁰ The mechanism of

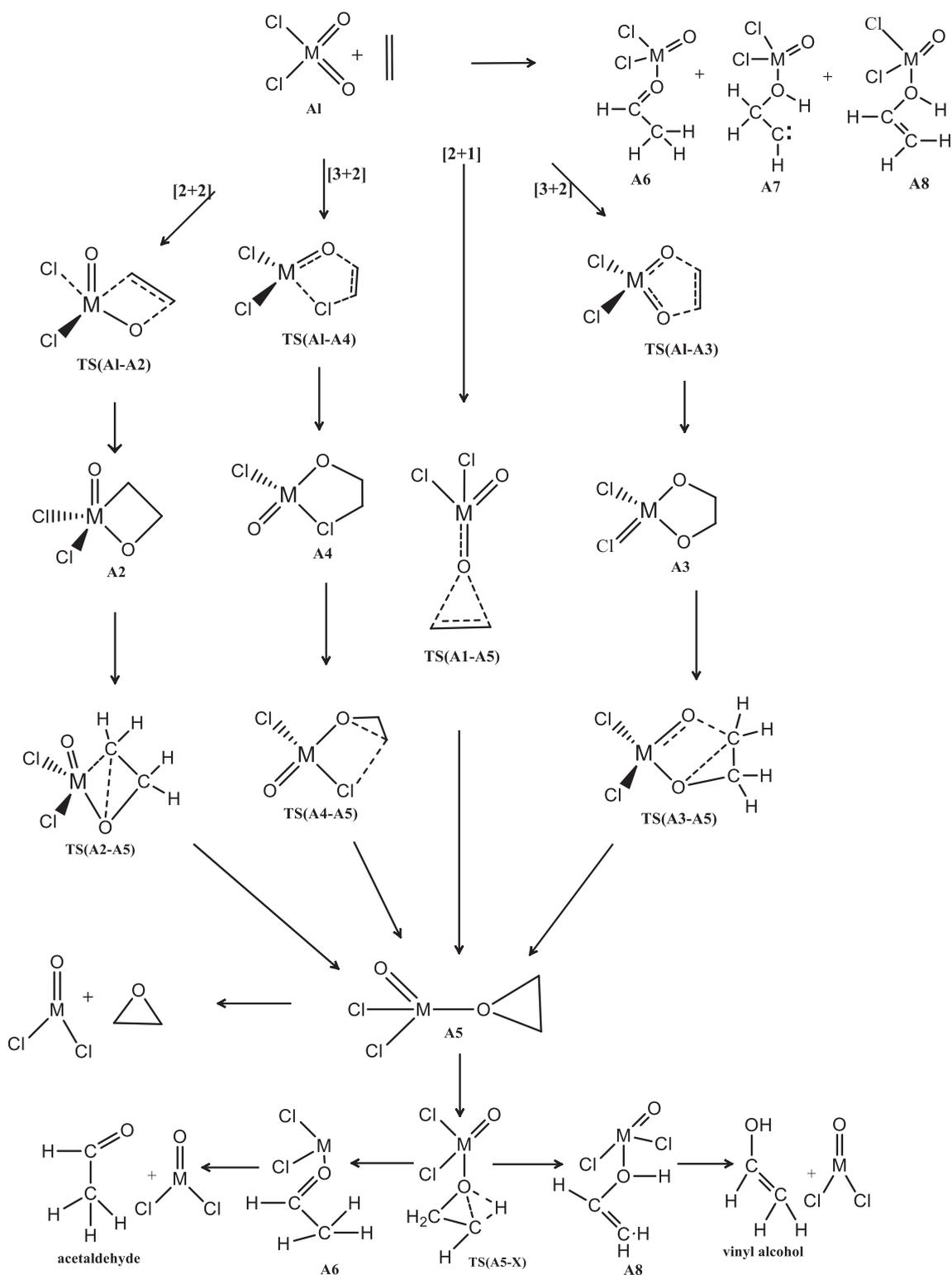
the oxidation of ethylene with MoO₂Cl₂ and WO₂Cl₂ leading ultimately to the formation of ethylene oxide (epoxide), 1,2-chlorohydrin, 1,2-dichloroethane, vinyl alcohol and acetaldehyde (schemes 3 and 4) was investigated theoretically using hybrid and meta-hybrid density functional theory. The calculations were carried out at both B3LYP and MO6 levels of theory and the results were compared to assess the performance of the two levels.

2. Computational Procedure

We performed all the computations with the Spartan²⁵ computational chemistry package developed by Wavefunction, Inc, versions 2008V1.2.0 and 2010V1.2.0, using the Becke-three-parameter Lee-Yang-Parr (B3LYP) hybrid exchange-correlational functional and the MO6 hybrid functional. The B3LYP functional, a Hartree-Fock DFT hybrid functional, is made up of the exchange-correlation energy from the local spin-density approximation (LSDA) method, 20% of the difference between the Hartree-Fock exchange energy (Kohn-Sham exchange energy) and the LSDA exchange energy, 72% of the Becke exchange potential (which includes the 1988 correction),^{26,27} 81% of the Lee-Yang-Parr correlation potential²⁸ and 19% of the Vosko-Wilk-Nusair potential²⁹ and is one of the most widely used exchange-correlation functionals in organometallic chemistry. The MO6 functional³⁰ is a global hybrid meta-generalized gradient approximation (meta-GGA) with 27% of Hartree-Fock exchange, leading to a well-balanced functional for overall good performance for chemistry. It has thus been recommended for application in organometallic and inorganometallic chemistry.³¹ The atoms hydrogen-chlorine were described with the 6-31G (d) basis set while the metals Mo and W were described with the lan12tz basis set.³²⁻³⁶

Spartan uses a graphical model builder for input preparation. Molecules were constructed and minimized interactively using an appropriate molecular mechanics force field. All structural optimizations were done without symmetry restrictions. Normal mode analysis was performed to verify the nature of the stationary points located. Minima, representing reactants, intermediates and products were shown to have no imaginary frequencies.

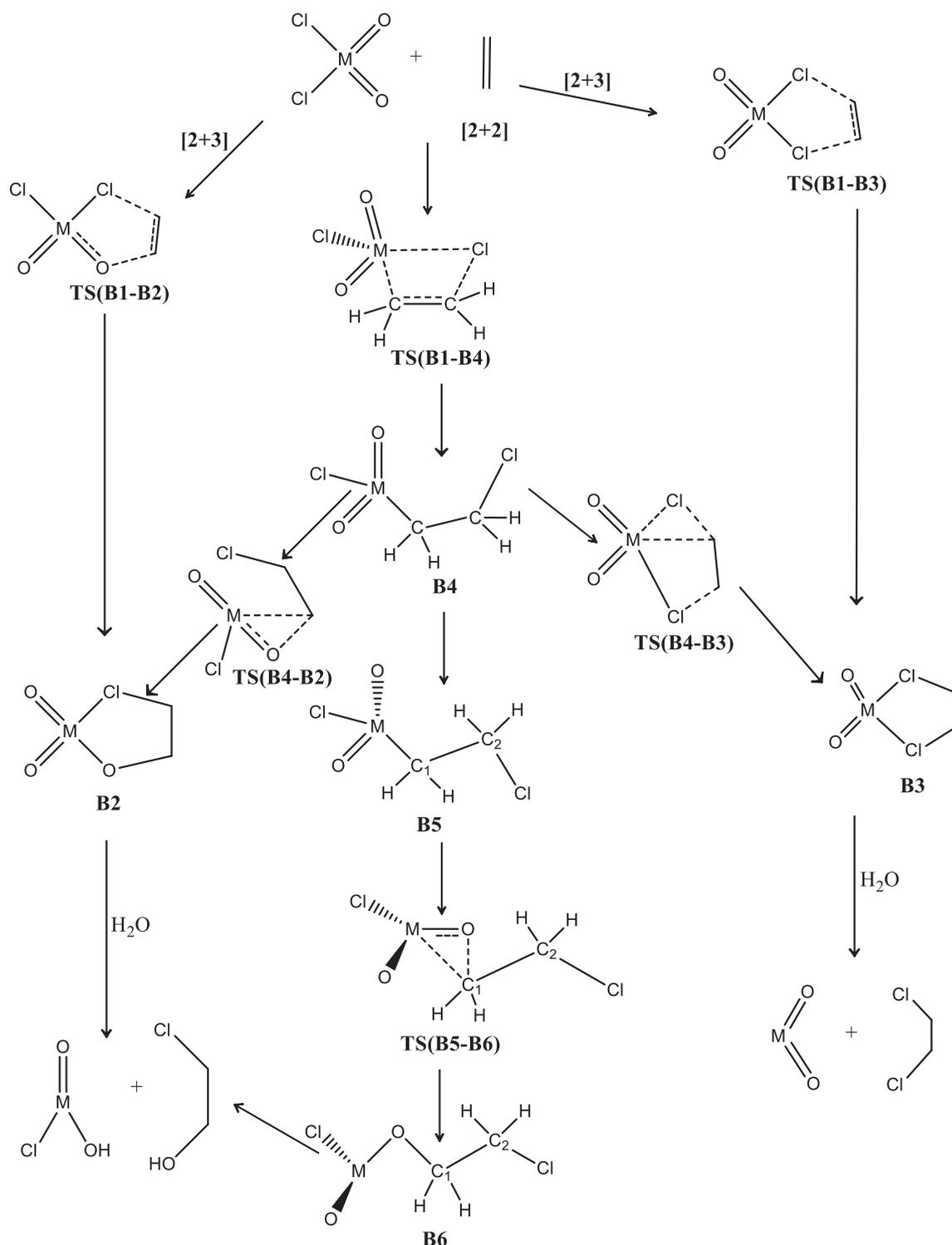
Guess structures for transition state calculations were obtained by first constraining specific bonds along the reaction coordinates at fixed lengths while the remaining internal coordinates were fully optimized. This procedure gives an approximate transition state guess



Scheme 3. Proposed mechanisms of the MO_2Cl_2 ($\text{M} = \text{Mo, W}$)-mediated formation of epoxide, acetaldehyde and vinyl alcohol.⁷

which is then submitted for transition state calculation using the standard transition state optimization procedure in Spartan. All transition state structures were subjected to full normal mode analyses to ensure that they have a Hessian matrix with a single negative

eigen-value, characterized by an imaginary vibrational frequency along the reaction coordinate. An intrinsic reaction coordinate (IRC) calculation was carried out to ensure that transition states smoothly connect reactants and products.



Scheme 4. Proposed mechanisms of the MO_2Cl_2 -mediated formation of chlorohydrins and dichlorides.⁷

3. Results and Discussion

3.1 Formation of the epoxide precursor

In the transformation of ethylene to the epoxide, the addition process can be viewed as that of a one oxygen atom transfer. From scheme 3, the metal center is involved in a reduction from d^0 in the reactant **A1**,

to d^2 in the products. A common direct precursor **A5** has been suggested in all the postulated mechanisms, no matter the pathway involved in the transformation. This species, first postulated by Sharpless *et al.*,³ as the immediate precursor of epoxide, was again proposed by Limberg *et al.*,^{37,38} also as the oxirane adduct intermediate leading to acetaldehyde.

From scheme 3, it is seen that species **A5** could in principle arise from four different pathways:

- (1) a two-step process involving initial [2 + 2] addition of ethylene across the M=O bond of MoO_2Cl_2 ;
- (2) a two-step process involving initial [3 + 2] addition of ethylene across the two oxygen atoms of MoO_2Cl_2 ;
- (3) a two-step process involving [3 + 2] addition of ethylene across the oxygen and chlorine atoms of MoO_2Cl_2 , and
- (4) a one-step direct addition of ethylene to one oxygen atom of MoO_2Cl_2 .

The [2 + 2] and [3 + 2] pathways are both two-step processes. The [2 + 2] involves a metalloxetane intermediate (**A2**) whereas the [3 + 2] pathway involves an ester complex intermediate (**A3**).

The energy profiles at the MO6 levels of theory are reported and discussed here. The profiles at the B3LYP level as well as the full set of optimized geometries for all the systems are reported in the Electronic Supplementary Information.

3.1a Molybdenum complex: The activation barrier for the formation of the molybdaoxetane by [2+2] addition through the metal-oxygen bond is 18.9 kcal/mol

(figure 1). In transition state **TS[A1-A2]**, the Mo-C forming-bond is almost completely formed whereas the C-O bond is still far from being formed. Therefore the critical bond activity in **TS[A1-A2]** is the formation of the C-O bond and this is seen in both the B3LYP and MO6 levels. The molybdaoxetane intermediate **A2** which results has an exothermicity of 0.4 kcal/mol on the singlet surface. Triplet **A2** is exothermic by 21.2 kcal/mol. Thus the triplet intermediate is far less stable than the singlet. The formation of the epoxide precursor **A5** from the molybdaoxetane intermediate **A2** through transition state **TS [A2-A5]** has an activation barrier of 41.3 kcal/mol and a reaction energy of $10.3 \text{ kcal mol}^{-1}$.

The [3 + 2] addition across the two oxygen atoms of molybdiyl chloride leads to the formation of a molybdadioxylate intermediate **A3** which is endothermic by 9.4 kcal/mol on the singlet and exothermic by 1.2 kcal/mol on the triplet surface. The geometry of the transition state at both levels of theory indicates a concerted and synchronous addition type. A comparison between the C-O bond lengths in the transition state and the product shows that it is an early transition state. The activation barrier for the [3 + 2] addition of ethylene across the O=M=O bonds of MoO_2Cl_2 is 30.2 kcal/mol and 44.3 kcal/mol on the singlet and

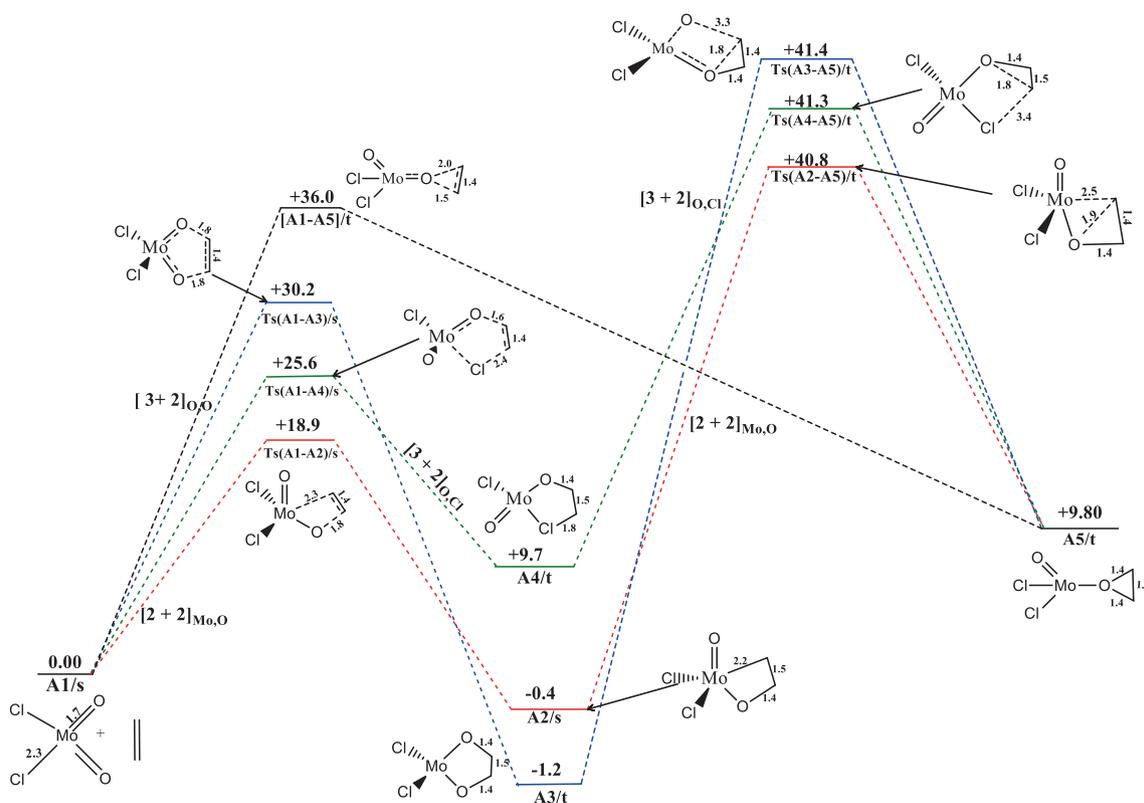


Figure 1. Reaction profile for the formation of the epoxide precursor from the addition of MoO_2Cl_2 and ethylene at MO6 level. There is spin cross-over intersystem crossing from the singlet reactant **A1/s** to the triplet epoxide precursor **A5/t** (s = singlet state, t = triplet). Energy in kcal/mol.

be less than 10 kcal/mol for the chromium adduct. The geometry of the transition state **TS [A1-A3]** at both levels of theory indicates a concerted and synchronous addition. A comparison between the C-O bond lengths in the transition state and the product shows that it is an early transition state. The ester complex intermediate **A3** is 27.0 kcal/mol and 53.4 kcal/mol endothermic on the singlet and triplet surfaces, respectively. The activation barrier and reaction enthalpy for the formation of the epoxide precursor **A5** from the ester complex are 44.5 kcal/mol and 12.2 kcal/mol, respectively. Triplet **TS [A1-A3]** was located at the MO6 to be 53.4 kcal/mol above the reactant while triplet **TS [A3-A5]** was 44.5 kcal/mol above the reactants. No triplet **TS[A1-A3]** and **TS[A3-A5]** was found at the B3LYP level.

Another pathway proposed for the formation of species **A5** is through the [3 + 2] addition across the O=W-Cl bonds of WO_2Cl_2 . At the MO6 level, the first step of this process has a barrier of 42.1 kcal/mol and the second step has a barrier of 24.7 kcal/mol. An exhaustive search on both the singlet and triplet PES at the B3LYP level however could not locate the structure **A4** but **TS [A1-A4]** was located on the triplet surface and found to be 56.0 kcal mol⁻¹.

This study indicates that even though in the first step of the epoxide precursor formation, the [2 + 2] addition across the W=O bonds is the most favorable pathway, conversion of the tungstaoxetane intermediate **A2** to the epoxide precursor involves a very high activation barrier and the epoxide precursor is therefore not likely to be formed from the tungstaoxetane intermediate. Also, the epoxide precursor is not likely to be formed from the direct [2 + 1] addition pathway due to the high energy barrier of 59.3 kcal/mol. From the two [3 + 2] addition pathways, both the first and second steps favor the [3 + 2] addition across the O=W-Cl bonds of WO_2Cl_2 . Hence if the epoxide forms at all, it will be formed by the [3 + 2] addition across the oxygen and chlorine atoms of WO_2Cl_2 since the highest energy barrier along this pathway is 42.1 kcal/mol as compared to 49.5 kcal/mol, 59.3 kcal/mol and 65.8 kcal/mol for the [3 + 2]_{O,O}; [2+1]_{O,Cl} and [2 + 2] pathways, respectively, at the MO6 level.

3.2 Formation of chlorohydrin and dichloroethane

Three mechanisms have been proposed for chlorohydrin precursor formation by Tia and Adei⁷ as shown in scheme 4. These are

- (a) a one-step reaction through [3 + 2]_{O,Cl} addition to form the chlorohydrin precursor (*i.e.*, **B2** in scheme 4);
- (b) a two-step reaction through [2 + 2]_{M,Cl} addition to form an intermediate **B4** which then undergoes re-arrangement to form the chlorohydrin precursor **B2** and
- (c) the formation of another chlorohydrin precursor **B6** from the re-arrangement of intermediate **B4** as shown in scheme 4.

The conversion of alkenes into 1,2-chlorohydrins was originally proposed by Sharpless *et al.*, (1977) to arise from cis-addition of the elements of HOCl across the C=C bond of the alkene, which is highly selective. Chlorohydrins arising from trans-addition were found to be secondary products derived by opening of the epoxide ring. Limberg *et al.*,^{37,38} also postulated the presence of $\text{CrOCH}_2\text{CH}_2\text{Cl}$ fragments in the Étard complex, which is consistent with the structure of **B6**, in a matrix isolation study of the reaction between CrO_2Cl_2 and ethylene. Scheme 4 also shows that the dichloride precursor could be formed by [3 + 2]_{Cl,Cl} addition of ethylene across the Cl-M-Cl bonds of the complexes.

3.2a Molybdenum complex: The activation barriers for the one-step [3 + 2] addition of ethylene across the oxygen and chlorine atoms of Cl_2MoO_2 is 25.6 kcal/mol on the singlet and 31.3 kcal/mol on the triplet (figure 3). Species **B2** is endothermic by 14.9 kcal/mol on the singlet and 9.7 kcal/mol on the triplet.

In the other one-step [3 + 2] addition across the two chlorine atoms for the formation of **B3** through **TS[B1-B3]**, neither the transition state **TS[B1-B3]** nor the dichloride precursor was located at the singlet and triplet PES for both B3LYP and MO6. The transition states **TS[B4-B2]** and **TS[B4-B3]** involved in the two-step formation of **B2** and **B3**, respectively, were not located after an exhaustive search.

Along the second proposed pathway for the formation of chlorohydrins in scheme 4, species **B5** which is 0.17 kcal/mol less stable than **B4** is formed when **B4** undergoes rotation about the C₁-C₂ bond. The energy barrier for the conversion of **B5** to the chlorohydrin precursor **B6** by the breaking of the Mo-C bond and the formation of the C-O bond is 55.84 kcal/mol on the singlet PES. Thus for the MoO_2Cl_2 , the preferred pathway for the chlorohydrin precursor is by concerted [3 + 2]_{O,Cl} addition.

3.2b Tungsten complex: In the one-step [3 + 2] addition across the two chlorine atoms for the formation of **B3** through **TS[B1-B3]**, both the singlet and triplet dichloride **B3** were located at B3LYP and MO6

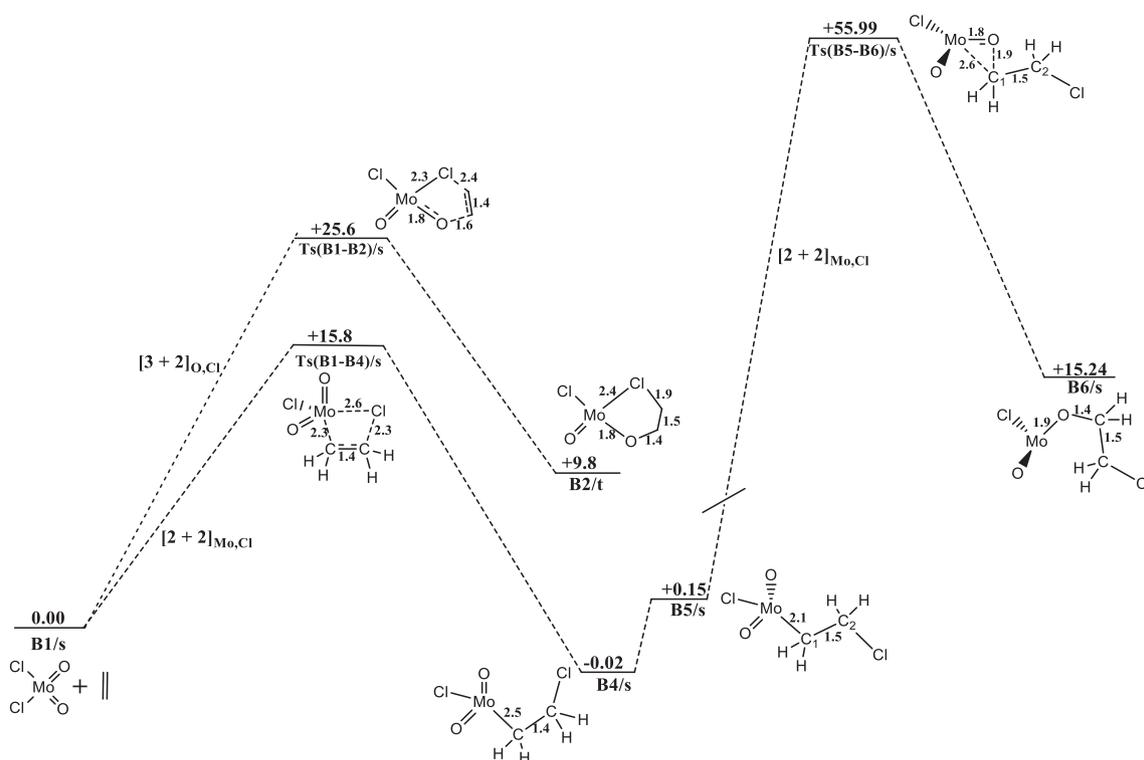


Figure 3. Reaction profile of mechanism for the formation of the 1,2-chlorohydrin precursor from the addition of MoO_2Cl_2 to ethylene at MO6. There is spin cross-over intersystem crossing from the singlet reactant **B1/s** to the triplet **B2/t** (s = singlet state, t = triplet). Energy in kcal/mol.

levels (figure 4) but transition state **TS [B1-B3]** linking the reactants to the precursor could be not located at either level. The singlet **B3** is 82.3 kcal/mol more stable than the separated reactants while the triplet **B3** is 86.6 kcal/mol more stable than the separated reactants but no transition state for its formation was located.

The activation barriers for the [3 + 2] addition across the oxygen and chlorine atoms, also a one-step process, are 42.1 kcal/mol and 52.9 kcal/mol, respectively, on the singlet and triplet surfaces. Furthermore, the product **B2** was found to be 40.0 kcal/mol and 36.4 kcal/mol endothermic on the singlet and triplet surfaces respectively. Also, the transition states involved in the two-step formation of **B2** and **B3** were not located in this study.

Along the third proposed pathway for the formation of chlorohydrins (scheme 4), species **B4** undergoes rotation about the $\text{C}_1\text{—C}_2$ bond to form species **B5** which is 0.2 kcal/mol less stable than **B4**. Species **B6**, which generates the chlorohydrin, is formed from **B5** by the breaking of the W-C bond and formation of the C-O bond. The energy barrier for this transition through **TS[B5-B6]** is 64.6 kcal mol⁻¹, with an endothermicity of 32.9 kcal/mol on the singlet surface. Thus the formation of a chlorohydrin precursor is not likely in the oxidation of ethylene with WO_2Cl_2 .

3.3 Formation of acetaldehyde and vinyl alcohol

Species **A5** was postulated by Limberg *et al.*,^{37,38} as the oxirane adduct intermediate leading to acetaldehyde, when the epoxide ring is opened. The products of the epoxide ring-opening were therefore localized on both the singlet and triplet potential energy surfaces.

3.3a Molybdenum complex: The singlet and triplet transition state **TS[A5-X]** for epoxide ring-opening were not obtained at both B3LYP and MO6. The singlet **A7** was 92.6 and 81.2 kcal/mol endothermic, at B3LYP and MO6 respectively. Triplet **A7** was not located at either the B3LYP or MO6. Species **A8**, which produces vinyl alcohol when it undergoes Mo-O single bond cleavage results from a 1,2-hydride shift from the secondary carbon to the terminal carbon of **A7**. At B3LYP and MO6, species **A8** was endothermic by 18.0 and 12.4 kcal/mol respectively on the singlet PES. The triplet **A8** has also been computed to be 5.6 kcal/mol exothermic at MO6 while no triplet **A8** was located at B3LYP. In an attempt to optimize **A8** on the singlet PES, the acetaldehyde precursor **A6** was obtained and was 3.7 and 10.8 kcal/mol exothermic for the singlet species, at B3LYP and MO6 respectively, making it the global minimum on the singlet PES at both levels

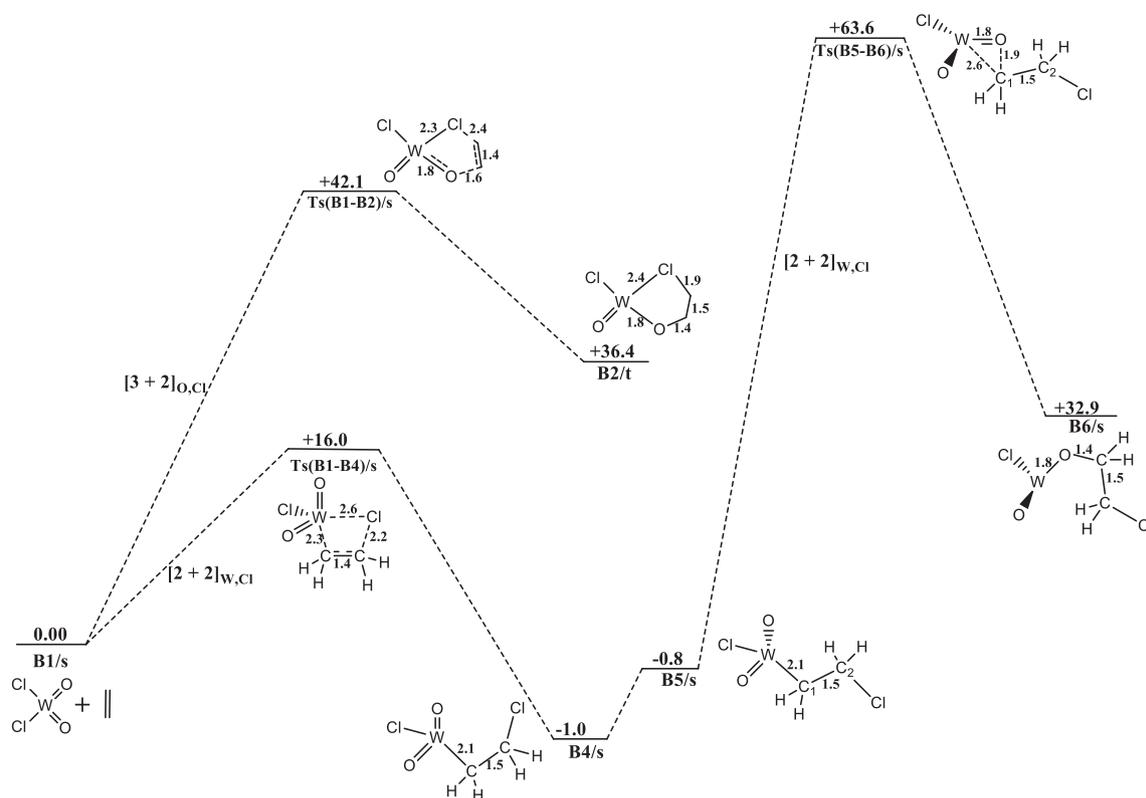


Figure 4. Reaction profile of mechanism for the formation of the 1,2-chlorohydrin precursor from the addition of WO_2Cl_2 to ethylene through the one step $[3 + 2]$ pathway at the MO6 level. There is spin crossover intersystem crossing from the singlet reactant **B1/s** to the triplet **B2/t** (s = singlet state, t = triplet). Energy in kcal/mol.

of theory. Furthermore, triplet **A6** was not obtained at either B3LYP or MO6. Thus oxidation with MoO_2Cl_2 may lead to acetaldehyde and vinyl alcohol.

3.3b Tungsten complex: The singlet and triplet transition state **TS [A5-X]** for epoxide ring-opening are respectively found to be 64.8 and 65.7 kcal/mol above the reactants at the B3LYP level but at the MO6 level, the singlet was not located but the triplet was found to be $58.9 \text{ kcal mol}^{-1}$. Tia and Adei had earlier observed⁷ that the transition state **TS [A5-X]** could lead to the formation of **A7** and that a 1,2-hydride shift from the secondary carbon to the terminal carbon of **A7** could result in species **A8**, which could undergo W-O single bond cleavage to produce vinyl alcohol. Triplet and singlet **A7** are 118.7 kcal/mol and 114.7 kcal/mol endothermic at B3LYP and 110.1 kcal/mol and 36.1 kcal/mol at MO6 levels, respectively. Species **A8** was computed to be 48.5 kcal/mol and 39.9 kcal/mol endothermic at the B3LYP level for singlet and triplet state respectively, and 43.4 kcal/mol and 63.0 kcal/mol endothermic for the singlet and triplet states respectively at the MO6 level of theory.

The acetaldehyde precursor **A6** has been obtained in optimizing **A8** on the PES. Species **A6** has energies of

20.1 and 22.6 kcal/mol for the singlet and triplet species respectively at B3LYP level and 17.6 kcal/mol and 17.6 kcal/mol on the singlet and triplet surfaces at the MO6 level. Limberg *et al.*,^{37,38} found **A6** an intermediate in the thermal reaction of ethylene with CrO_2Cl_2 and postulated it as a precursor to the formation of acetaldehyde, upon cleavage of the Cr-O single bond. Thus the formation of acetaldehyde and vinyl alcohol from the oxidation with WO_2Cl_2 does not appear energetically feasible.

3.4 Comparison of the reactions of chromyl chloride, molybdyl chloride and tungstyl chloride with ethylene

Table 1 shows a comparison of the activation barriers of the various elementary reaction steps in the oxidation of ethylene with chromyl chloride, molybdyl chloride and tungstyl chloride. It is seen that the oxyhalides MO_2Cl_2 become weaker oxidants in the order $\text{CrO}_2\text{Cl}_2 \gg \text{MoO}_2\text{Cl}_2 > \text{WO}_2\text{Cl}_2$. Corresponding to this, reactions involving reduction of the metal show a sharp increase in barrier going from Cr to W: this applies to the $[3 + 2]$ and $[2 + 1]$ reactions in table 1. On the other and, reactions without a change in metal oxidation state ($[2 + 2]$) show much smaller variations,

Table 1. Activation barriers of the various elementary reaction steps in the oxidation of ethylene with chromyl chloride, molybdenyl chloride and tungstyl chloride^{a,b}.

| Complex | Activation barriers of reaction steps (kcal/mol) | | | | | | | |
|----------------------------------|--|-----------------------|----------------------|-----------------------|-------|-------|-------|-------|
| | [3 + 2] _{O,O} | [3+2] _{O,Cl} | [2+2] _{M,O} | [2+2] _{M,Cl} | [2+1] | A3→A5 | A2→A5 | A4→A5 |
| Cl ₂ CrO ₂ | 8.8 | 9.0 | 26.3 | 25.6 | - | 46.9 | 13.4 | 41.3 |
| Cl ₂ MoO ₂ | 30.2 | 25.6 | 18.9 | 15.8 | 36.0 | 42.6 | 41.3 | 31.6 |
| Cl ₂ WO ₂ | 49.5 | 42.1 | 16.9 | 16.0 | 59.3 | 44.5 | 65.9 | 24.7 |

^aData for the Cr complex from ref. ⁷ ^bEnergetics of the Cr complex at B3LYP level and for the Mo and W at MO6 level.

which are possibly mainly determined by sterics (reactions around Cr would suffer from steric congestion). It is seen that the barriers of the concerted [3 + 2]_{O,O} and [3 + 2]_{O,Cl} addition increase down the group 6 elements from Cr through Mo to W while the barriers for the [2 + 2]_{M,O} addition decrease down the group, making the formation of the dioxylate more favourable in Cr and the formation of the metallaoxetane more favourable in W. For each of the complexes the barriers of the [3 + 2]_{O,O} and [3 + 2]_{O,Cl} are close but the [3 + 2]_{O,Cl} route becomes more favoured as the group is descended. It is also seen that the conversion of the dioxylate intermediate to the epoxide precursor is not a very feasible step in any of the complexes. Also, while the barriers of the [2 + 2]_{M,O} addition decrease down the group, the barriers for the conversion of the resulting metallaoxetane to the epoxide precursor increase sharply down the group, offsetting the feasibility of the formation of the epoxide precursor through initial [2 + 2]_{M,O} addition. This makes the Cr complex the only complex where the epoxide precursor may arise from the initial [2 + 2]_{M,O} addition even though that initial step has the highest barrier in the Cr complex.

4. Conclusion

The formation of an epoxide from the oxidation of ethylene with MoO₂Cl₂ and WO₂Cl₂ is not a very feasible process by any of the postulated pathways. If the epoxide precursor forms at all, it will arise *via* initial [3 + 2]_{O,Cl} addition of ethylene across the O=M-Cl bonds of MoO₂Cl₂ and WO₂Cl₂ to form an intermediate, followed by re-arrangement to form the precursor (Cl₂(O)M-OC₂H₄), from which the epoxide can be generated by hydrolysis. The chlorohydrin precursor will originate from [3 + 2]_{O,Cl} addition of ethylene across the O=M-Cl bonds of MO₂Cl₂. The results also indicate that a dichloride is not a likely product in the oxidation of ethylene by molybdenyl chloride as none of the postulated intermediates, transition states and precursors for its formation have been located. However, in

the case WO₂Cl₂ though no transition states could be located, a very stable dichloride precursor is formed, indicating that the formation of a dichloride may not be precluded. The formation of acetaldehyde and vinyl alcohol from the oxidation of ethylene does not appear energetically feasible with MoO₂Cl₂, but appears thermodynamically plausible with WO₂Cl₂. Thus, the oxidation of ethylene with MoO₂Cl₂ will most likely lead to the formation of chlorohydrins predominantly *via* [3 + 2]_{O,Cl} addition; oxidation with WO₂Cl₂ may also form chlorohydrins, but only extremely slowly. Comparing these results with those of CrO₂Cl₂ reported earlier by us, it is seen that the oxyhalides MO₂Cl₂ become weaker oxidants in the order CrO₂Cl₂ >> MoO₂Cl₂ > WO₂Cl₂. Corresponding to this, reactions involving reduction of the metal show a sharp increase in barrier going from Cr to W: this applies to the [3 + 2] and [2 + 1] reactions. On the other and, reactions without a change in metal oxidation state ([2 + 2]) show much smaller variations, which are possibly mainly determined by sterics (reactions around Cr would suffer from steric congestion). There are a number of singlet-triplet spin crossover in the course of the oxidation reactions studied, showing the importance of multiple spin states in this class of organometallic reactions. The MO6 and B3LYP functionals have been found to give similar activation barriers for most of the steps but the MO6 predicts more stable intermediates and products than the B3LYP.

Supplementary Information

Energy profiles and optimized geometrical parameters of all the stationary points involved in the reactions reported. Figures S1–S16 are available as Supplementary Information at www.ias.ac.in/chemsci.

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and JE ran calculations and analyzed data. RT and EA wrote the manuscript.

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