



Permanganyl chloride-mediated oxidation of tetramethylethylene: A density functional theory study

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ABSTRACT

The mechanisms of the oxidation of tetramethylethylene (TME) by permanganyl chloride (MnO_3Cl) have been explored on the singlet and triplet potential energy surfaces at the B3LYP LANL2DZ/6-31G (d) level of theory. The results show that the pathway leading to the formation of the five-membered dioxylate through concerted [3 + 2] addition is favored kinetically and thermodynamically over the three other possible pathways, namely the [2 + 2] addition via the transient metallaoxetane intermediate, epoxidation, and hydrogen transfer pathways. The epoxide precursor that on hydrolysis would yield the epoxide product will most likely arise from a stepwise path through the intermediacy of an organo-metallic intermediate. This pathway affords the product that is more stable (thermodynamically favorable). However, kinetically, both the stepwise and the concerted [2 + 1] addition pathways leading to the epoxide precursors are very competitive (activation barrier difference of <0.7 kcal/mol).

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1. Introduction

The advancement of novel catalyzed chemical reactions which achieve high selectivity and catalytic efficiency remains a grand challenge. Several of such novel reactions are serendipitous, but increased understanding of the reaction mechanism in terms of the kinetics and intermediate stabilities at the molecular level permits the control and design of new compounds.

Transition metal-oxo complexes such as MnO_4^- , OsO_4 , MnO_3Cl and CrO_2Cl_2 are oxidation catalysts and chiefly involved in reactions where oxygen is added across olefinic double bond. The use of such oxidation catalysts in chemical research has stimulated huge interest in the fundamental reaction mechanisms [1–4]. For example, CrO_2Cl_2 undergoes a reaction with ethylene to form products such as epoxide, chlorohydrin and vicinal dihalides [5,6] while MnO_4^- and OsO_4 catalysts are reported to form only diols [7,8]. Theoretical and experimental studies focusing on the mechanisms of oxidation of alkenes like ethylene by transition metal oxo complexes of the type MO_3L have widely been explored [9–16]. For instance, in MnO_4^- and OsO_4 , the mechanism of oxidation of alkenes are reported to be similar, although donor and acceptor olefins differently

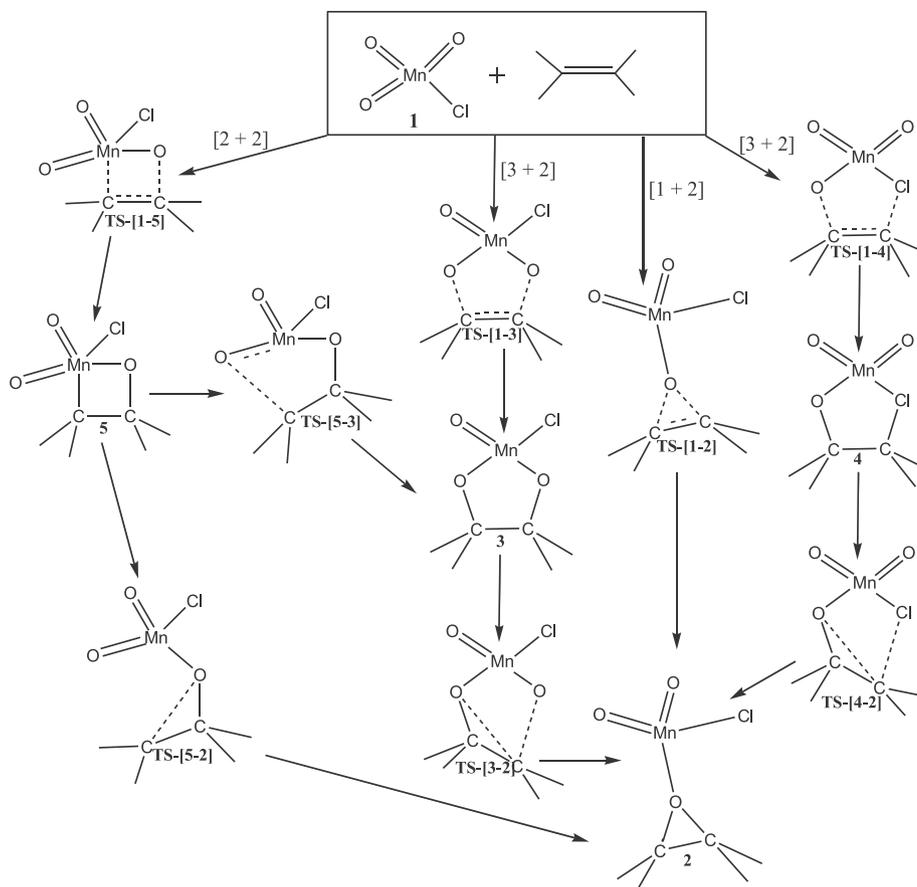
influence the rate of reactions from OsO_4 to MnO_4^- as a result of net charge difference.

In the oxidation of ethylene catalyzed by MnO_4^- , the initial step involving the [3 + 2] addition of the ethylene with the $\text{O}=\text{Mn}=\text{O}$ moiety of MnO_4^- to form a metalladioxolane, a five-membered metallacycle [17] (3, Scheme 1) was reportedly favored, until Sharpless et al. [18] postulated the intermediacy of metallaoxetane in an analogous reaction of chromyl chloride catalyzed epoxidation of alkenes. However, the metallaoxetane intermediate (5, Scheme 1) arising from the direct [2 + 2] addition pathway as evidenced by oxidation of alkene by chromyl chloride, was dismissed for permanganate (MnO_4^-), through density functional theory (DFT) calculations by Houk et al. [16] and further supported experimentally by kinetic isotope effect [15,19].

Aniagyei et al., [12–14] in a theoretical study, reported the mechanisms of oxidation of alkene catalyzed by metal oxo complexes of the type MO_3L ($\text{M} = \text{Mn, Tc and Re}$; $\text{L} = \text{O}^-, \text{Cl}^-, \text{Cp, CH}_3, \text{OCH}_3, \text{NPH}_3$). It was observed that on the singlet surface, the dioxylate intermediates formed from the [3 + 2] addition pathways were primarily the most favored for the Mn, Tc and Re complexes. The activation barriers and product stabilities for the Tc and Re complexes followed the trend: $\text{O}^- > \text{CH}_3 > \text{NPH}_3 > \text{CH}_3\text{O}^- > \text{Cl}^- > \text{Cp}$. For the Mn system, the dioxylate formed from [3 + 2] addition pathway had the activation barrier and product stabilities follow the trend: $\text{NPH}_3 < \text{Cl}^- < \text{CH}_3\text{O}^- < \text{Cp} < \text{O}^- < \text{CH}_3$. This is

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Scheme 1. Proposed pathway for the reaction of MnO_3Cl with ethylene and tetramethylethylene.

contrary to the observed trends in Tc and Re systems. They reported that for all the systems studied, the best epoxidation catalyst would be the Cl^- ligand on the singlet surface, while the probable dioxylating catalyst would be Cp ligand for both Tc and Re systems. For the Mn system, $\text{MnO}_3(\text{OCH}_3)$ catalyst was reported to yield only dioxylate.

For permanganyl chloride catalyzed oxidation of tetramethylethylene (TME), Wistuba et al. [20] reported the direct [3 + 2] pathway leading to the formation of the dioxylate intermediate to be the most favored thermodynamically, when compared to the epoxidation product from the direct [2 + 1] addition pathway. However, at the B3LYP LANL2DZ/6-311G (d) level of theory, Wistuba reported both reactions to be of equal kinetic heights. Nevertheless, in an experiment to study TME– MnO_3Cl system by low temperature photolytic matrix isolation technique, the epoxidation product $\text{ClO}_2\text{MnO}[\text{C}(\text{CH}_3)_2]_2$ was only formed. The epoxide product was characterized by infra-red spectroscopy coupled with isotopic-enrichment experiment. The effects of permethylation on these barriers were not accurately calculated and were ignored by way of assumptions based on results obtained for an analogous ethylene system partly due to the fact that detailed investigation of the TME system is computationally expensive.

The main aim of the paper is to extend the earlier theoretical work of Wistuba et al. [20] by exploring the potential energy surfaces for the permanganyl chloride catalyzed oxidation of tetramethylethylene at the B3LYP LANL2DZ/6-31G (d) level of theory at $T = 193.15$ K and $P = 0.00001$ atm. The initial first step leading to the formation of the four- and five-membered metallacycles, the interconversion of the four- to five-membered metallacyclic

intermediate and their subsequent rearrangement to the epoxide precursors (Scheme 1) are investigated. Several organometallic reactions have been reported to exist in several spin states and surfaces [5,12–14,21]. The bond lengths, angular distortions and molecular geometry are affected by change of spin states. For organometallic transformations, cross effects of the spin can impart the reaction mechanisms [22]. As a result, the singlet and triplet states in C_1 symmetry which are possible have been considered in all the calculations reported in this paper.

2. Details of calculation

The density functional/Hartree-Fock hybrid model B3LYP [23–26] as implemented in Gaussian 09 [27] has been used throughout this study together with the basis set of LanL2DZ for manganese atoms while the split valence double- ζ (DZ) [28] 6-31G (d) for the non-metal atoms (H, C, O and Cl). Molecular structures were generated with Avogadro software [29]. 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 which is then submitted for transition state calculation using the standard transition state optimization procedure in Gaussian 09. 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. Approximate free energies were obtained through thermochemical analysis of the frequency calculation, using the thermal correction to Gibbs free energy as reported by Gaussian 09. This takes into account zero-point effects, thermal enthalpy corrections, and entropies. All energies reported in this paper, unless otherwise noted, are free energies at 193.15 K and pressure of 0.00001 atm using unscaled frequencies. This is because the reactions of permanganyl chloride with olefins cannot be induced at temperatures below 50 K [20]. All energies are given in kcal/mol relative to the reactants.

3. Results and discussion

3.1. Reaction of MnO_3Cl with tetramethylethylene

The relative energies of the main stationary points involved in the reactions between MnO_3Cl and tetramethylethylene (TME) are shown in Fig. 1. The thermal-corrected absolute Gibbs free energies and Cartesian coordinates of the reactants and intermediates are shown in Table S1 and S2 while the optimized geometries in the reaction of permanganyl chloride and tetramethylethylene (TME) reported herein are given in Fig. S1 in the ESI[†]. On the singlet potential energy surface, MnO_3Cl , the starting reactant, generated two minima: one with C_3V symmetry labelled as **R1-A1/s** and other minima with $C_S</SUB>$ symmetry labelled as **R2-A1/s**. **R1-A1/s** has been computed to be 36.6 kcal/mol more stable than **R2-A1/s** and 22.7 kcal/mol more stable than the triplet reactant **A1/t**. Hence, **R1-A1/s** was chosen as the reactant in all subsequent reactions.

Although, B3LYP/6-31G* has been reported in several studies [5,12–14,30] to be a reliable combination of functional and basis set for organometallic compounds, a larger basis set may sometimes be needed to evaluate a flat potential energy surface [31]. Wistuba et al. [20] optimized the structures of the potential products at the B3LYP LANL2DZ/6-311G (d) level of theory. Notwithstanding, at the larger basis of B3LYP LANL2DZ/6-311G (d), the singlet structure, **R1-A1/s** lies 22.4 kcal/mol lower in energy than the triplet state **A1/t**.

The formation of **A3/s** is exergonic (−43.3 kcal/mol) with the corresponding free activation barrier for the [3 + 2] transition state calculated being 0.2 kcal/mol. On the triplet PES, **A3/t** lies 14.4 kcal/mol lower than **A3/s**. The geometry of the transition state **TS-[A1-A3]/s** is symmetrical with bond lengths of 2.40 Å for the forming bonds between the MnO_3Cl oxygens and the TME substrate. **A3/t** lies 34.8 and 29.0 kcal/mol lower in energy than the singlet (**A2/s**) and triplet (**A2/t**) epoxide precursors. However, an exhaustive attempt to locate the transition state linking the reactant to the product on the triplet surface proved futile. Wistuba et al. [20] in their theoretical studies of TME catalyzed by MnO_3Cl at the B3LYP LANL2DZ/6-311G (d) level of theory at $T = 293.15$ K and $P = 0.001$ atm, found **A3/t** lies 13.4 kcal/mol lower than **A3/s**. Also, they reported **A3/t** to lie 33.0 and 27.5 kcal/mol lower in energies than the singlet (**A2/s**) and triplet (**A2/t**) epoxide precursors. Their results agree with our free energies calculations at B3LYP LANL2DZ/6-311G (d) level of theory at $T = 193.15$ K and $P = 0.00001$ atm. However, the formation of the dioxylate by the direct [3 + 2] addition reaction is kinetically favored over both the concerted and stepwise [2 + 1] addition reactions leading ultimately to the formation of the epoxide precursor. At 293.15 K and $P = 0.001$ atm, Wistuba et al. [20] reported both kinetic barriers for epoxidation and dihydroxylation reactions to be of comparable height. Although, it is worth commenting that the two theoretical reactions were calculated under different conditions, the choice of the basis set in this paper is less critical, since the basis set does not

change the product stabilities or improved energetics. Herein, all intermediates and transition state structures were optimized at the B3LYP LANL2DZ/6-311G (d) level of theory.

Also, the [3 + 2] addition of the $C=C$ π bond of TME across the $O=Mn-Cl$ bonds of MnO_3Cl on the singlet surface leads to product **A4/s**. However, the transition state connecting the reactants to the product on the singlet and triplet PES could not be located. Formation of **A4/s** is also exergonic (16.1 kcal/mol). In the triplet product **A4/t**, the $Mn-Cl$ bond in the five-membered metallacycle is broken. **A4/t** is 7.4 kcal/mol more stable than **A4/s**.

The stepwise [2 + 2] route via a transition state and a transient metallaoxetane intermediate, which according to sharpless et al. [18] re-arranges to the [3 + 2] product (Scheme 1) was also explored. In the [2 + 2] case, the free energy of activation (40.2 kcal/mol) for the singlet transition state is high. This leads to singlet (12.9 kcal/mol) and triplet (23.0 kcal/mol) intermediates which are unstable compared to corresponding intermediates for the [3 + 2] pathway, but obviously want to stay on the singlet surface. The endergonic formation of **A5** via a transition state that has free activation energy of 40 kcal/mol makes this competing pathway highly improbable and will not be significantly populated. Additionally, the thermodynamically most stable species **A3/t** is exergonic by more than 44.8 kcal/mol. Therefore, we did not investigate the rearrangement transition states leading from the metallaoxetane to the cyclic ester product.

The formations of **A6/s** and **A6/t** are exergonic (23.6 and 40.8 kcal/mol) with an associated free activation energy of 16.1 kcal/mol. The calculated free activation energy is significantly lower when compared to those leading to the formation of **A5/s**. No transition state were located on the triplet surface after an exhaustive search. In the process of formation of **A6/s** in the transition state, the $C-O$ bond remains intact but the $Mn-C$ bond (3.06 Å) cleaves, with simultaneous transfer of a hydrogen atom from a methyl group on the olefin to an oxo ligand leading ultimately to the formation of a hydroxyl group at the metal centre.

Also, compound **A7/s** resulted from the attack of one methyl substituent on the olefin on the oxo group at the metal centre and concomitant hydrogen transfer to the oxo group leading to the formation of hydroxyl at the metal centre. The free energies for the formation of **A7** on the singlet (−27.1 kcal/mol) and triplet (−42.0 kcal/mol) **A7** are exergonic, with **A7/t** being 14.9 kcal/mol more stable than **A7/s**. The transition state connecting the reactants to the product on the singlet and triplet PES were not be located after exhaustive searches. Wistuba et al. [20] at the B3LYP LANL2DZ/6-311G (d) level of theory at $T = 293.15$ K and $P = 0.001$ atm reported that **A7/t** lies 14.0 kcal/mol lower than **A7/s** in agreement to our calculated free energies for **A7/s** and **A7/t** at 193.15 K and 0.00001 atm.

3.2. Formation of epoxide precursors

Wistuba et al. [20] reported that in the experimental investigation of the TME/ MnO_3Cl system by means of matrix isolation techniques, selective formation of the epoxidation product was observed. For the oxidation of ethylene by manganese–oxo complexes of the type MnO_3L ($L = O^-, Cl^-, CH_3, OCH_3, Cp, NPH_3$), Aniagyei et al. [14] reported that the best epoxidation catalyst for the Mn complexes is MnO_3Cl and the formation of the epoxide precursor will not result from the reaction of MnO_3L ($L = O^-$ and Cp) with ethylene on any of the surfaces studied. The main focus of this paper was therefore to identify the epoxide precursor that on hydrolysis would yield the epoxide, which was reported to be the major product reaction of MnO_3Cl with TME by Wistuba et al. [20].

The formation of the epoxide precursor through the direct [2 + 1] addition of the $C=C$ π bond of TME across one oxo ligand of

MnO₃Cl through transition state **TS-[A1-A2]/s** has free activation barrier of 8.0 kcal/mol. The singlet **A2/s** and triplet **A2/t** epoxide precursors along this pathway are exergonic by 22.9 and 28.7 kcal/mol respectively. The triplet epoxide precursor **A2/t** is 5.8 kcal/mol more stable than the singlet.

Also, the epoxide precursor could be accessed from the rearrangement of **A3/s** through transition state **TS-[A3-A2]/s**. The free activation barrier along this route is 47 kcal/mol and free energy of the epoxide precursor formation through this route is 18.2 kcal/mol.

Along the stepwise pathway, one of the C=C π bonds of TME attacks an oxo-ligand of MnO₃Cl to form the organometallic intermediate **X/s**. The free activation barrier for the formation of **X/s** is 8.7 kcal/mol. Intermediate **X/s** formed from the stepwise pathway is endergonic (2.4 kcal/mol). In the subsequent step, **X/s** then rearranges through transition state **TS-[X-A2]/s** to form **A2/s** with free activation barrier of -4.3 kcal/mol (Fig. 1). The free energy for the formation of the singlet and triplet epoxide precursors through this stepwise route are -25.3 and -31.1 kcal/mol respectively. The transition state **TS-[X-A2]/s** being below the entry channel and

therefore giving slightly negative activation barriers could most likely be that the transition state was preceded by a weak π -complex (which we looked for but did not find) or as a result of the basis set superposition error as reported by Haunschild et al. [32] for the reactions of RhO₂(CH₃)CH₂ with ethylene.

Since in the matrix isolation experiment by Wistuba et al. [20] selective formation of the epoxide was observed, the epoxide precursor will most likely arise from a stepwise pathway because of the product stability (thermodynamically favorable) as compared to the product distribution formed through the rearrangement of **A3/s**. However, kinetically, both the stepwise re-arrangement pathway and the direct [2 + 1] addition route are competitive (difference of only 0.7 kcal/mol).

4. Conclusion

The first step of the [3 + 2] addition leading to the formation of the **A3/s** and **A3/t** are kinetically and thermodynamically the most favored pathway in the MnO₃Cl and TME reaction; it is favored over all other pathways explored in this study. Wistuba et al. [20] in their

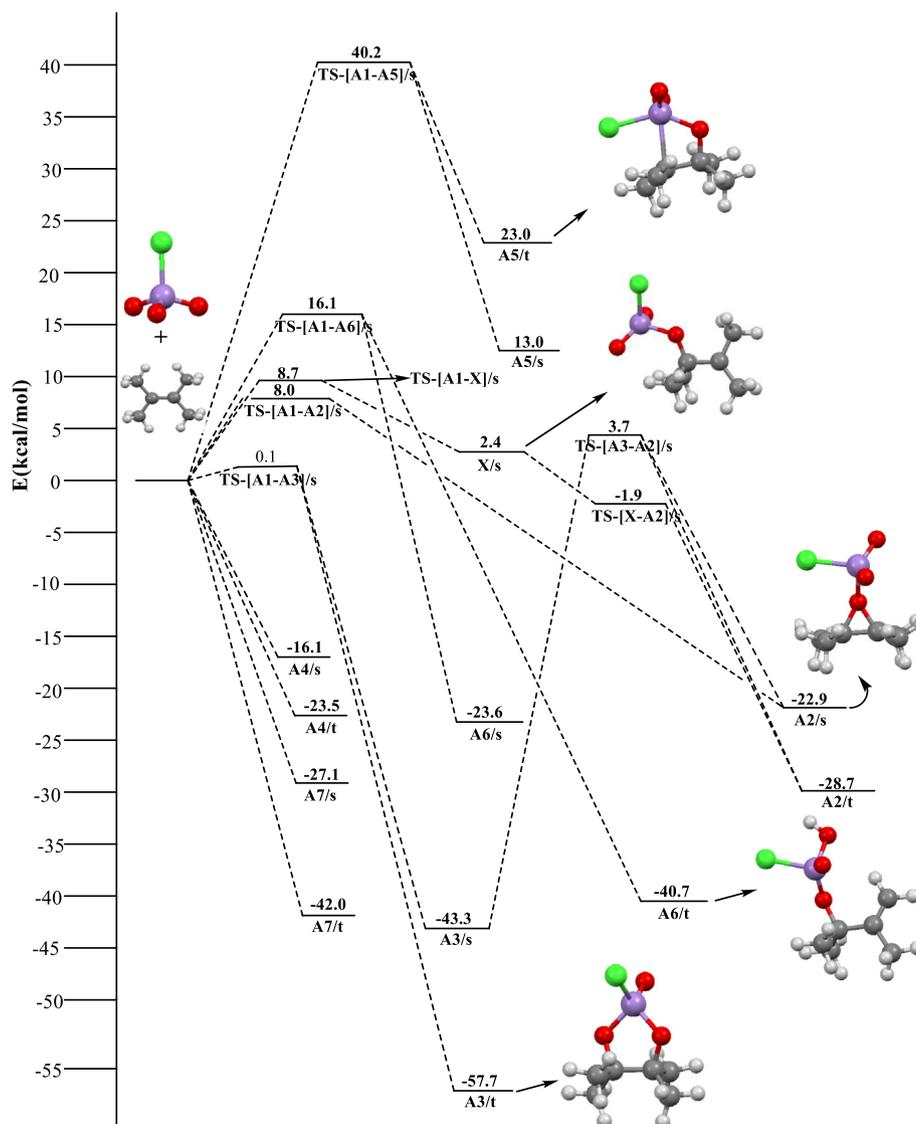


Fig. 1. Thermal corrected Gibbs free energies profile of the addition of MnO₃Cl with TME B3LYP LANL2DZ/6-31G (d) level of theory (T = 193.15 K and P = 0.00001 atm). All relative energies in kcal/mol. Colour code: green = Cl, Grey = C, purple = Mn, white = H and red = O.

theoretical studies of TME catalyzed by MnO₃Cl at the B3LYP LANL2DZ/6-311G (d) level of theory at T = 293.15 K and P = 0.001 atm reported the kinetic barriers for both epoxidation and dihydroxylation reactions are of comparable height. The epoxide precursor that on hydrolysis would yield the epoxide will most likely arise from the stepwise organometallic intermediate. This pathway affords the product that is more stable (thermodynamically favorable). However, kinetically, both the stepwise and the direct [2 + 1] addition route pathways are very competitive (<0.7 kcal/mol).

Also, the stepwise [2 + 2] route via a transient metallaoxetane intermediate, which according to Sharpless et al. [18] re-arranges to the dioxylate, is not competitive with the epoxidation or dihydroxylation reactions. The endergonic formation of the metallaoxetane state that is on the average 40 kcal/mol, makes this competing pathway highly improbable and will not be significantly populated.

Declaration of competing interest

The authors declare that there is no conflict of interests whatsoever regarding the publication of this manuscript.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jmngm.2020.107616>.

References

- [1] J.H. Enemark, C.G. Young, Bioinorganic chemistry of pterin-containing molybdenum and tungsten enzymes, *Adv. Inorg. Chem.* 40 (1993) 1–88.
- [2] K.B. Sharpless, K. Akashi, Oxidation of alcohols to Aldehydes by reagents derived from chromyl chloride, *J. Am. Chem. Soc.* 97 (1975) 5927–5928.
- [3] W. Mijs, C.R. Jonge, *Organic Synthesis by Oxidation with Metal Compound*, Plenum, New York, 1986.
- [4] M. Sono, M.P. Roach, E.D. Coulter, H.E. Dawson, Heme-containing oxygenases, *Chem. Rev.* 96 (1996) 2841–2888.
- [5] R. Tia, E. Adei, Density functional theory study of the mechanism of oxidation of ethylene by chromyl chloride, *Inorg. Chem.* 48 (2009) 11434–11443.
- [6] J. San Filippo, C. Chern, Chemisorbed chromyl chloride as a selective oxidant, *J. Org. Chem.* 42 (1977) 2182–2183.
- [7] M. Schröder, Osmium tetraoxide cis-hydroxylation of unsaturated substrates, *Chem. Rev.* 80 (1980) 187–213.
- [8] K.B. Wiberg, *Oxidation in Organic Chemistry*, Academic Press, New York, 1965, pp. 1–68.
- [9] S. Dapprich, G. Ujaque, F. Maseras, A. Lledos, D.G. Musaev, K. Morokuma, Theory does not support an osmaoxetane intermediate in the osmium-catalyzed dihydroxylation of olefins, *J. Am. Chem. Soc.* 118 (1996) 11660–11661.
- [10] U. Pidun, C. Boehme, G. Frenking, Theory rules out a [2 + 2] addition of osmium tetraoxide to olefins as initial step of the dihydroxylation reaction, *Angew. Chem., Int. Ed. Engl.* 35 (1996) 2817–2820.
- [11] M. Torrent, L. Deng, M. Duran, M. Solà, T. Ziegler, Density functional study of the [2 + 2] and [2 + 3] cycloaddition mechanisms for the osmium-catalyzed dihydroxylation of olefins, *Organometallics* 16 (1997) 13–19.
- [12] A. Aniagyei, R. Tia, E. Adei, A density functional theory study of the mechanisms of oxidation of ethylene by rhenium oxide complexes, *Dalton Trans.* 42 (2013) 10885–10897.
- [13] A. Aniagyei, R. Tia, E. Adei, A density functional theory study of the mechanisms of oxidation of ethylene by technetium oxo complexes, *Comp. Theor. Chem.* 1009 (2013) 70–80.
- [14] A. Aniagyei, R. Tia, E. Adei, A theoretical study of the mechanisms of oxidation of ethylene by manganese oxo complexes, *Dalton Trans.* 42 (2013) 14411–14423.
- [15] A.J. Del Monte, J. Haller, T. Strassner, K.N. Houk, Experimental and theoretical kinetic isotope effects for asymmetric dihydroxylation, evidence supporting a rate-limiting [3 + 2] cycloaddition, *J. Am. Chem. Soc.* 119 (1997) 8031–8034.
- [16] K.N. Houk, T. Strassner, Establishing the [3 + 2] mechanism for the permanganate oxidation of alkenes by theory and kinetic isotope effects, *J. Org. Chem.* 64 (1999) 800–802.
- [17] (a) R. Criegee, Osmiumsauer-ester als Zwischenprodukte bei Oxydationen, *Justus Liebig's Ann. Chem.* 522 (1936) 75–96; (b) R. Criegee, B. Marchaand, H. Wannowius, Zur Kenntnis der organischen Osmium-Verbindungen. II. Mitteilung, *Ann. Chem.* 550 (1942) 99–133.
- [18] K.B. Sharpless, A.Y. Teranishi, J.E. Bäckvall, Chromyl chloride oxidations of olefins. Possible role of organometallic intermediates in the oxidations of olefins by oxo transition metal species, *J. Am. Chem. Soc.* 99 (1977) 3120–3128.
- [19] A. Dauth, J.A. Love, Reactivity by design—metallaoxetane as centerpieces in reaction development, *Chem. Rev.* 111 (2011) 2010–2047.
- [20] T. Wistuba, C. Limberg, Reaction of permanganyl chloride with olefins: intermediates and mechanism as derived from matrix-isolation studies and density functional theory calculation, *Chem. Eur. J.* 21 (2001) 4674–4685.
- [21] J.N. Harvey, R. Poli, K.M. Smith, Understanding the reactivity of transition metal complexes involving multiple spin states, *Coord. Chem. Rev.* 238–239 (2003) 347–361.
- [22] D. Schröder, S. Shaik, H. Schwarz, Two-state reactivity as a new concept in organometallic chemistry, *Acc. Chem. Res.* 33 (2000) 139–145.
- [23] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, *Phys. Rev. B Condens. Matter* 37 (1988) 785–789.
- [24] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M. Frisch, Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields, *J. Phys. Chem.* 98 (1994) 11623–11627.
- [25] S.H. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis, *Can. J. Phys.* 58 (1980) 1200–1211.
- [26] A.D. Becke, A new mixing of Hartree-Fock and local density-functional theories, *J. Chem. Phys.* 98 (1993) 5648–5652.
- [27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, K. Toyota, J. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford CT, 2009.
- [28] A. Schäfer, C. Huber, R. Ahlrichs, Fully optimized contracted Gaussian basis sets for atoms Li to Kr, *J. Chem. Phys.* 100 (1994) 5829.
- [29] M.D. Hanwell, D.E. Curtis, D.C. Lonie, T. Vandermeersch, E. Zurek, G.R. Hutchison, An advanced semantic chemical editor, visualization, and analysis platform, *J. Cheminf.* 4 (1) (2012).
- [30] G. Frenking, I. Antes, M. Boehme, S. Dapprich, A.W. Ehlers, V. Jonas, A. Neuhaus, M. Otto, R. Stegmann, A. Veldkamp, S.F. Vyboishchikov, in: K.B. Lipkowitz, D.B. Boyd (Eds.), *Reviews in Computational Chemistry*, vol. 8, VCH, New York, 1996, pp. 63–144.
- [31] T. Strassner, K.N. Houk, Mechanism of permanganate oxidation of Alkanes: hydrogen abstraction and oxygen “rebound”, *J. Am. Chem. Soc.* 122 (2000) 7821.
- [32] R. Haunschild, G. Frenking, Ethylene addition to group-9 transition metal dioxo compounds – a quantum chemical study, *Z. Anorg. Allg. Chem.* 634 (2008) 2145–2155.