



Exploring the peri-, chemo-, and regio-selectivity of addition of manganese metal oxides MnO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) to substituted ketenes: A computational study



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ABSTRACT

Ketenes are interesting reactive intermediates that find a wide range of synthetic applications. Density functional theory calculations at the MO6/LACVP* and B3LYP/LACVP* levels of theory have been employed to explore the peri-, chemo-, and regio-selectivity of the addition of manganese oxo complexes MnO_3L ($\text{L} = \text{Cl}$, O^- , OCH_3 , CH_3) to substituted ketenes $\text{O}=\text{C}(\text{CH}_3)(\text{X})$ [$\text{X} = \text{H}$, CH_3 , Cl , CN , Ph] with the aim of elucidating the effects of substituents on the mechanism of the reactions. The results show that the concerted [3+2] addition of the C=C bond of the ketene across the metal complex is the most preferred pathway in all the reactions studied (with respect to changing ligand L on the metal complex or substituent X on the ketene) except in the reaction of MnO_4^- (i.e. for $\text{L} = \text{O}^-$) with dimethyl ketene, which follows only a stepwise addition pathway. [2+2] addition is found to be possible only in the reaction of $\text{MnO}_3-\text{OCH}_3$ with dimethyl ketene where the activation barrier for [2+2]_{C=O} addition is 23.79 kcal/mol, which is far greater than the barrier for the [3+2] addition. The reactions of dimethyl ketene with MnO_4^- will most likely lead to the formation of an ester precursor and the reaction of MnO_3Cl with the substituted ketenes would lead to the formation of an ester precursor, chlorohydrin precursor, acetaldehyde and carbon monoxide (for $\text{X} = \text{H}$, Cl). Generally, reactions involving an increase in oxidation state of metal have higher activation barriers. For both [3+2] and [2+2] addition, low activation barriers are obtained when the substituent on the ketene is electron-donating while high activation barriers are obtained when the substituent is electron-withdrawing. The reactions of ketenes with MnO_3L complexes have lower activation barriers for the preferred [3+2] and [2+2] addition pathways as well as fewer side reactions than those of the ReO_3L complexes reported in the literature, a trend which was seen in our earlier work with reactions of group VII metals with olefins, implying that manganese oxo complexes efficiently and selectively catalyze specific reactions in oxidation of ketenes and olefins than do Re oxo complexes and therefore Mn oxo complexes may be better catalysts for specific oxidation reactions of ketenes and olefins than Re complexes are.

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1. Introduction

Oxidation of ketenes by metal oxides has recently received considerable interest. Ketenes are important reactive intermediates [1–6], which have found a wide of applications in synthetic chemistry ranging from the Staudinger synthesis of β -lactams to the photochemical Wolff rearrangement. Ketenes are known to be outstanding precursors for catalytic asymmetric reactions mainly through addition across their C=C bonds. They readily react with nucleophiles to form zwitterionic enolates that form the basis

for much of asymmetric chemistry. Researchers have productively utilized ketenes in a range of reaction manifolds, including cycloadditions, reductive couplings, nucleophilic $\text{S}_{\text{N}}2$ substitutions, as well as both electrophilic and nucleophilic additions.

Research is still ongoing towards the development of new catalytic reactions that enhance chemical transformations with high selectivity and efficiency, to enable the conversion of reactants to products in a cost-effective manner. Research over the decades has shown that transition-metal catalyzed processes have high selectivity and efficiency.

Deubel and co-workers [1] studied addition of metal oxides OsO_4 and ReO_3L ($\text{L} = \text{O}^-$, H_3PN , Me , Cp) to simple ketenes using density-functional methods [1] which showed that the barriers for the [2+2] addition (across the C=C or C=O bond of the simple

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ketenes depending on the ligand of the metal oxide) are the lowest compared to the [3+2] barriers. The study also indicated that the reaction of the metal oxides with diphenylketene follow a different mechanism than the reactions of simple ketenes. The diphenylketene reaction follows a two-step pathway: a zwitterionic intermediate is formed and subsequently cyclizes to form a four- or five-membered ring metallacycle.

Experimental works have been carried out involving the reaction of the metal oxide Re(VII) complex trioxo(η^5 -pentamethylcyclopentadienyl)rhenium $[(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_3]$ with excess diphenylketene in tetrahydrofuran (THF) at room temperature which formed a violet carbocyclic cycloadduct [2] rapidly and nearly quantitatively. This adduct was characterized to be a five-membered ring formed through [3+2] cycloaddition. This work [2] also indicated that the marked oxyphilicity of rhenium in higher oxidation states $[(\eta^5\text{-C}_5\text{Me}_5)\text{ReO}_2]$ allows two types of reaction to occur, a [3+2] and [2+2] cycloaddition across the C=C and C=O bonds, respectively. [2+2] cycloaddition across the C=O moiety of the ketene to give the four-membered ring was found to occur only when the metal center is capable of attaining an even higher coordination number. Middleditch et al. [3] in their experimental works obtained a series of [3+2] products (isolated six novel [3+2] cycloaddition products) in the reactions of rhenium (VII) trioxo complexes containing the ligand sets scorpionate, $[\text{HB}(\text{pz})_3]\text{ReO}_3$, $[\text{Ph-B}(\text{pz})_3]\text{ReO}_3$, and $[\{\text{HC}(\text{pz})_3\}\text{ReO}_3][\text{ReO}_4]$ and pyridine/pyridine-type ligands $[(4,7\text{-diphenyl-1,10-phen})(\text{Br})\text{-ReO}_3]$, $[(4,4'\text{-di-tert-butyl-2,2'-dipyridyl})(\text{Cl})\text{ReO}_3]$, and $[(\text{py})_2\text{Re}(\text{Cl})\text{O}_3]$, with diphenyl ketene.

A recent work by Ahmed et al. [4] on the peri-, chemo-, and regio-selectivity of the addition of transition metal oxo complexes of the type ReO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) to substituted ketenes $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ [$\text{X} = \text{CH}_3$, H , CN , Ph] showed that the [2+2] addition pathway (across the C=C or C=O depending on the ligand) is the most preferred in the reactions of dimethyl ketene with all the metal complexes studied. This is consistent with the works of Deubel et al. [1]. The [2+2] pathway is also the most preferred in the reactions of ReO_3Cl with all the substituted ketenes studied except when $\text{X} = \text{Cl}$ which is chemo selective towards [3+2] addition pathway. The work [4] indicated that reactions involving an increase in oxidation state of metal from the reactant to product have high activation barriers while reactions that do not involve a change in oxidation state have low activation barriers. It was demonstrated in this study that these reactions have the potential to afford dioxiranes precursors, CO_2 , chlorohydrins precursor and esters (lactone).

The question of whether the oxidation of ketenes by metal oxo complexes would give kinetically and thermodynamically favored intermediate and/or products is not only of academic interest. Transition metal-oxo compounds and oxo-halides such as such CrO_2Cl_2 , OsO_4 , MnO_4 , ReO_4^- and RuO_4^- are applied extensively in reactions in which oxygen is inserted into C–H bonds or undergoes addition to a C=C double bond. The application of such reagents in chemical synthesis has spurred considerable interest in the underlying activation mechanism [7–15].

Even though several theoretical and experimental works on ketene have been carried out with Re oxo complexes, no work had been conducted with respect to the lower homologs like Mn. Studies involving oxidation of alkenes by Re, Tc and Mn oxo complexes indicates that the formation of the similar analogs through [3+2] or [2+2] addition pathway favors the Mn oxo complexes kinetically and thermodynamically [7–9]. We present the first theoretical study on the addition of Mn oxo complexes to ketenes. The peri-, chemo-, and regio-selectivity of the addition of transition metal oxo complexes of the type MnO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) to substituted ketenes $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ [$\text{X} = \text{CH}_3$, H , CN , Ph] is explored by hybrid density functional theory at the B3LYP/LACVP* and MO6/

LACVP* level of theory, by considering the most viable [3+2] and [2+2] addition pathways and for the interconversion of the four- or five-membered intermediates to esters. The work also seeks to compare LMnO_3 to LReO_3 reactions with ketenes and explore the effect of substituent on the mechanism of addition of MnO_3L across the C=C and C=O bonds. This is done according to the scheme developed in Ref. [4] for the Re complexes (Schemes 1 and 2). This is an exploratory predictive mechanistic study aimed at investigating the various plausible pathways for ketene reactions with manganese oxo complexes. The results will be useful in the design of manganese oxo complexes as catalysts for the selective oxidations of substituted ketenes, beyond the reported ReO_3L complexes.

2. Details of calculation

All computations were performed with Spartan'08 V1.2.0 and Spartan'10 V1.1.0 Molecular Modeling programs [16] at the DFT B3LYP/LACVP* and MO6/LACVP* levels of theory. The B3LYP functional [17–19] is a Hartree–Fock DFT hybrid functional. The MO6 is meta-hybrid exchange–correlation that has been recommended by Zhao and Truhlar for application in organometallic and inorganometallic chemistry [20]. The LACVP* basis set is a relativistic effective core-potential that describes the atoms H–Ar with the 6-31G(d) basis while heavier atoms are described with the LANL2DZ basis set which uses Dunning's all-electron valence double zeta basis set (D95V), for first row elements and the Los Alamos ECP plus double zeta basis set of Wadt and Hay for the atoms Na–La, Hf–Bi [21–24].

The starting geometries of the molecular systems were constructed using Spartan's graphical model builder and minimized interactively using the sybyl force field [25]. All geometries were fully optimized without any symmetry constraints. A normal mode analysis was performed to verify the nature of the stationary point. Equilibrium geometries were characterized by the absence of imaginary frequencies.

The transition state structures were located by a series of constrained geometry optimizations in which the forming- and breaking-bonds are fixed at various lengths while the remaining internal co-ordinates will be optimized. The approximate stationary points located from such a procedure were then fully optimized using the standard transition state optimization procedure in Spartan. All first-order saddle-point will be shown to have a Hessian matrix with a single negative eigenvalue, 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.

3. Results and discussion

The study is in two main sections. Sections 3.1.1–3.1.4 look at the reactions of MnO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) with dimethyl ketene. Sections 3.2.1–3.2.4 look at the reactions of MnO_3Cl , the least selective of the Mn complexes explored here, with a series of substituted ketenes $\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$ [$\text{X} = \text{H}$, CH_3 , Cl , CN , Ph]. This will help elucidate the effects of substituents on the mechanism of the reactions.

3.1. Reactions of MnO_3L ($\text{L} = \text{Cl}^-$, O^- , OCH_3 , CH_3) with dimethyl ketene

3.1.1. Reaction of MnO_3Cl with dimethyl ketene

Fig. 1 shows the relative energies of the reactants, transition states, intermediates and products involved in the reaction between MnO_3Cl and dimethyl ketene and some of the optimized

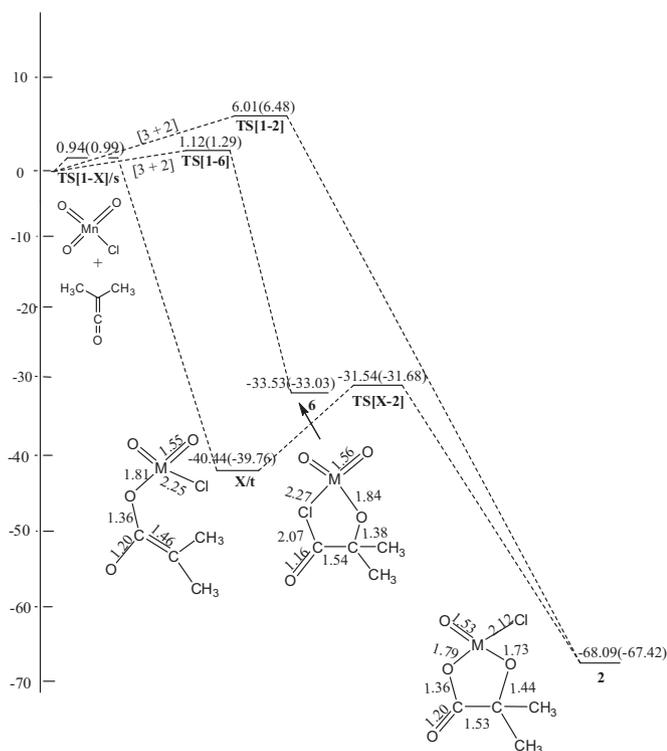


Fig. 1. Energetics of the reaction of MnO_3Cl with dimethyl ketene on the singlet PES at the B3LYP level of theory. Energies in kcal/mol. Zero-point corrected energies in parentheses.

structures. The singlet structure of MnO_3Cl is 22.40 kcal/mol more stable than the triplet structure when both species were computed as neutral structures. On the singlet potential energy surface (PES), the concerted [3+2] addition of the $\text{O}=\text{Mn}=\text{O}$ bond of the metal oxide across the $\text{C}=\text{C}$ bond of the ketene to form metalla-2,5-dioxolane-4,4-dimethyl-3-one species **2** (Fig. 1) through transition state **TS-[1-2]** has an activation barrier of 6.01 kcal/mol and exothermicity of 68.09 kcal/mol at the B3LYP level of theory and activation barrier of 3.18 kcal/mol and exothermicity 72.45 kcal/mol at the MO6 level.

As seen in Scheme 2, the formation of species **2** could also arise from a stepwise pathway as a result of spin crossover from the singlet reactants **1a** and **1b** through a singlet transition state **TS-[1-X]**s to form a triplet zwitterionic intermediate **X/t** with a very low activation barrier of 0.94 kcal/mol and exothermicity of 40.44 kcal/mol at the B3LYP level of theory. The triplet zwitterionic intermediate **X/t** then re-arranges through singlet transition state **TS-[X-2]**s to form species **2/s** with energy barrier of 8.90 kcal/mol and exothermicity of 27.65 kcal/mol at the B3LYP level of theory.

The concerted [3+2] addition of the $\text{O}=\text{Mn}=\text{Cl}$ bond of the metal oxide across the $\text{C}=\text{C}$ bond of the ketene to form the five-membered metallacycle **6** (Fig. 1) on the singlet PES has an activation barrier of 1.12 kcal/mol and exothermicity of 33.53 kcal/mol at the B3LYP level of theory while at the MO6 level of theory the barrier is 0.72 kcal/mol and exothermicity of 35.49 kcal/mol, respectively. No [2+2] addition pathway is located on this PES unlike in the case of ReO_3Cl [10] where [2+2] addition occurs for all the metal oxides.

The most plausible addition pathway on this PES is the concerted [3+2] addition of the $\text{O}=\text{Mn}=\text{Cl}$ bond of the metal oxide across the $\text{C}=\text{C}$ of the ketene to form the five-membered metallacycle species **6** with activation energy of 1.12 kcal/mol. This is in contrast to the reaction of the ReO_3Cl with dimethyl ketene [4] where the most plausible addition pathway is the concerted

[2+2] addition of the $\text{Re}=\text{O}$ bond of the metal oxide across the $\text{C}=\text{C}$ of the ketene with activation energy of 13.64 kcal/mol.

The activation energies involved in the reaction of MnO_3Cl with dimethyl ketene are relatively lower than those in the reactions of ReO_3Cl with dimethyl ketene [4] for the same reactions. Also Mn is also more selective than Re since there are fewer feasible reaction pathways in the reactions of MnO_3Cl than in ReO_3Cl . The chemical reactivity, particularly of the higher homologs, is influenced by the increasing strength of relativistic effects which is in the order $\text{Mn} < \text{Tc} < \text{Re}$ [26]. This points out to the fact that compounds containing first row transition metals often show a different reactivity compared to their higher homologs which is consistent with the work of Frenking and Haunschild [26,27] where the first row transition metal Co exhibited different chemical reactivity compared to the higher homologs Rh and Ir.

The calculated activation and reaction energies for addition pathways (Table 1) at the MO6 level of theory are lower than those at the B3LYP, which is consistent with the work of Linder and Brinck [28] and Ahmed et al. [4] but both levels predict the same preferred addition pathways and the same trends.

3.1.2. Reaction of MnO_4^- with dimethyl ketene

Fig. 2 shows the optimized geometries and the energy profile of the reaction between MnO_4^- and dimethyl ketene and the energetics of the reactions are shown in Table 2. The singlet structure of MnO_4^- is 22.30 kcal/mol more stable than the triplet structure; when both species were computed as anionic structures.

No [2+2] or [3+2] concerted addition pathway is identified towards the formation of four- or five-membered ring metallacycle either across the $\text{C}=\text{C}$ or $\text{C}=\text{O}$ of the ketene. This is unlike the reported Re oxides where at least one [2+2] or [3+2] concerted addition pathway is found either across the $\text{C}=\text{C}$ or $\text{C}=\text{O}$ bond of the ketene. This again points to the fact that the Mn being the first row metal exhibits different chemical reactivity.

One stepwise pathway is located towards the formation of the singlet zwitterionic species **X** through transition state **TS-[1-X]** with activation energy -0.83 kcal/mol (which becomes 0.24 kcal/mol with the inclusion of zero-point vibrational energy correction) and reaction energy of -9.35 kcal/mol at the B3LYP level of theory. The negative activation barrier could be attributed to the basis set superposition error just as was seen in the works of Frenking and Haunschild [24] and the works of Aniygyei et al. [9] in the oxidation of olefins with Rh and Mn oxides, respectively. The singlet zwitterionic species **X** goes through cyclization through transition state of **TS-[X-2]** to form five-membered metallacycle species **2** with activation barrier of 1.94 kcal/mol and exothermicity of 66.61 kcal/mol at the B3LYP level of theory. It also cyclizes through transition state **TS-[X-3]** to form the three membered ring lactone (Fig. 2). The energies involved are much lower for the Mn than Re for similar reactions [4].

Table 1

Calculated activation energies and reaction energies in kcal/mol for some selected addition pathways in the reaction of $\text{MnO}_3\text{-Cl}$ with dimethyl ketene at the B3LYP and MO6 levels of theory.

Chlorine ligand		Activation energy		Reaction energy	
Reaction path	Addition	B3LYP	MO6	B3LYP	MO6
1 → 2	[3+2] _{C=C}	6.01 (6.48)	3.18 (3.48)	-68.09 (-67.42)	-72.45 (-70.56)
1 → 6	[3+2] _{C=C}	1.12 (1.29)	0.72 (0.84)	-33.53 (-33.03)	-35.79 (-34.63)
1 → X	[1+1]	0.94 (0.99)	0.58 (0.69)	-40.44 (-39.76)	-45.68 (-43.87)
X → 2	Re-arrangement	8.90 (8.08)	5.16 (5.85)	-27.65 (-27.66)	-30.12 (-29.48)

Zero-point corrected energies in parentheses.

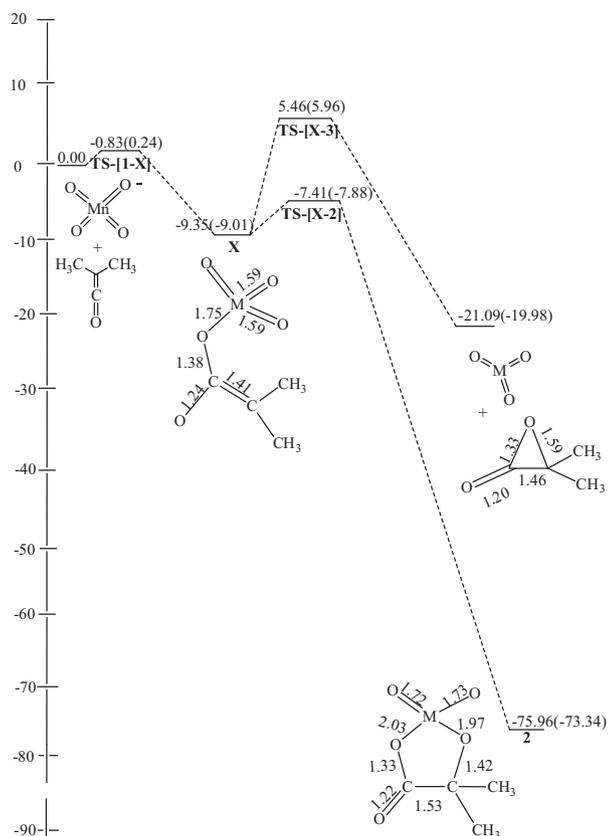


Fig. 2. Energetics of the reaction of MnO_4^- with dimethyl ketene on the singlet PES at the B3LYP level of theory. Energies in kcal/mol. Zero-point corrected energies in parentheses.

The calculated energy barriers for the formation of similar analog species **2** (Fig. 2) have lower barriers compared to chlorine ligand (Fig. 1). Also, the reaction of the MnO_4^- with dimethyl ketene is highly selective compared to that of the MnO_3Cl . The high selectivity of MnO_4^- than MnO_3Cl agrees with earlier works on the ReO_4^- complex [4]. The ability of MO_4^- ($\text{M} = \text{Mn, Re, Tc}$) to catalyze the oxidation of olefins selectively to fewer products was noted in the work of Aniagyei et al. [7–9] where MnO_4^- , ReO_4^- and TcO_4^- reactions with ethylene had lower barriers for fewer reaction pathways leading to high selectivity.

3.1.3. Reaction of $\text{MnO}_3\text{-OCH}_3$ with dimethyl ketene

The optimized geometries and the energy profile of the reactions of $\text{MnO}_3\text{-OCH}_3$ with dimethyl ketene is shown Fig. 3 with the energetics summarized in Table 3. The singlet structure of

Table 2

Calculated activation energies and reaction energies in kcal/mol for some selected addition pathways in the reaction of MnO_4^- with dimethyl ketene at the B3LYP and MO6 level of theories.

Reaction	Oxygen ligand	Addition	Activation energy		Reaction energy	
			B3LYP	MO6	B3LYP	MO6
1 → X		[1+1]	-0.83 (0.24)	0.46 (0.54)	-9.35 (-9.01)	-11.44 (-10.89)
X → 2		Re- arrangement	1.94 (1.13)	0.78 (0.97)	-66.61 (-64.33)	-80.14 (-78.50)
X → 3		Re- arrangement	14.81 (14.97)	8.41 (8.97)	-11.74 (-10.97)	-13.18 (-12.98)

Zero-point corrected energies in parentheses.

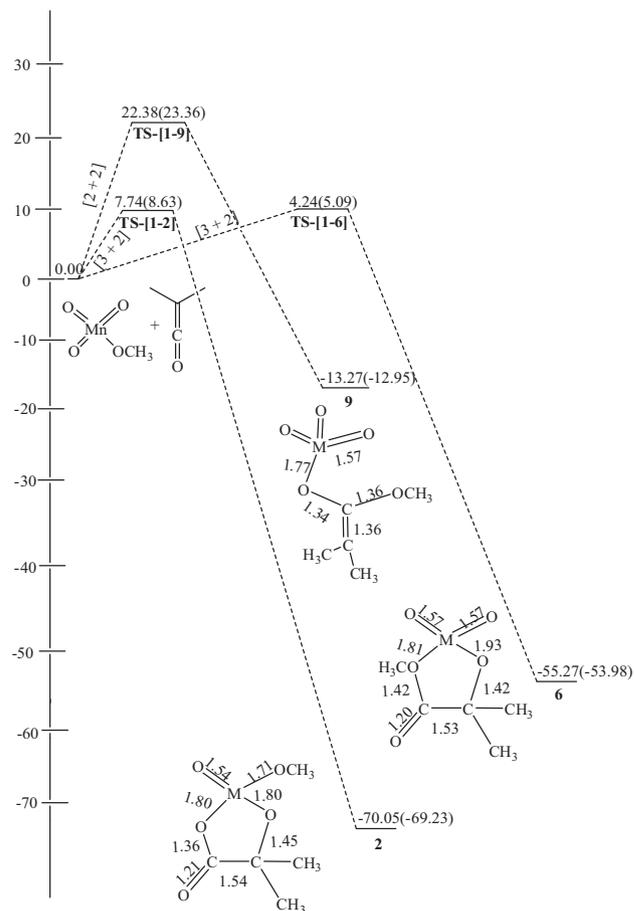


Fig. 3. Energetics of the reaction of $\text{MnO}_3\text{-OCH}_3$ with dimethyl ketene on the singlet PES at the B3LYP level of theory. Energies in kcal/mol. Zero-point corrected energies in parentheses.

Table 3

Calculated activation and reaction energies in kcal/mol for the addition pathways in the reaction of $\text{TcO}_3\text{-OCH}_3$ with dimethyl ketene at the B3LYP and MO6 levels of theory.

Reaction	Methoxy ligand	Addition	Activation energy		Reaction energy	
			B3LYP	MO6	B3LYP	MO6
1 → 2		[3+2] _{C=C}	7.74 (8.63)	4.36 (4.79)	-70.05 (-69.23)	-76.18 (-75.04)
1 → 6		[3+2] _{C=C}	4.24 (5.09)	2.98 (3.32)	-55.27 (-53.98)	-60.93 (-57.92)
1 → 9		[2+2] _{C=O}	22.38 (23.36)	14.71 (15.84)	-13.27 (-12.95)	-16.84 (-14.08)

Zero-point corrected energies in parentheses.

$\text{MnO}_3\text{-OCH}_3$ is 21.13 kcal/mol more stable than the triplet structure when both species are computed as neutral structures. The concerted [3+2] addition of the $\text{O}=\text{Mn}=\text{O}$ bond of the metal oxide across the $\text{C}=\text{C}$ bond of the ketene to form metalla-2,5-dioxolane-4,4-dimethyl-3-one on the singlet PES species **2**, (Fig. 3) through a transition state **TS-[1-2]** has an activation energy of 7.74 kcal/mol and exothermicity of 70.05 kcal/mol at the B3LYP level of theory. The MO6 level of theory gives an activation barrier of 4.36 kcal/mol and reaction energy of -76.18 kcal/mol.

The formation of species **9** (Fig. 3) through concerted [2+2] addition of the $\text{M}-\text{OCH}_3$ bond of the metal oxide across the $\text{C}=\text{O}$ of the ketene to form an open shell intermediate species **9** has activation barrier of 22.38 kcal/mol with exothermicity of

13.27 kcal/mol at the B3LYP level of theory. The preference of the [3+2] over the [2+2] is consistent with the work of Herrmann [2], Middleditch [3] and Ahmed et al. [4].

The most plausible addition pathway on this PES is the concerted [3+2] addition of the O=Mn–OCH₃ bond of the metal oxide across the C=C of the ketene to form the five-membered metallacycle species **6** with activation energy of 4.24 kcal/mol. This is in contrast to the reaction of the ReO₃–OCH₃ with dimethyl ketene [4] where the most plausible addition pathway is the concerted [2+2] addition of the Re=O bond of the metal oxide across the C=C of the ketene to form the open shell intermediate species **5** (Scheme 1) with activation barrier of 10.38 kcal/mol.

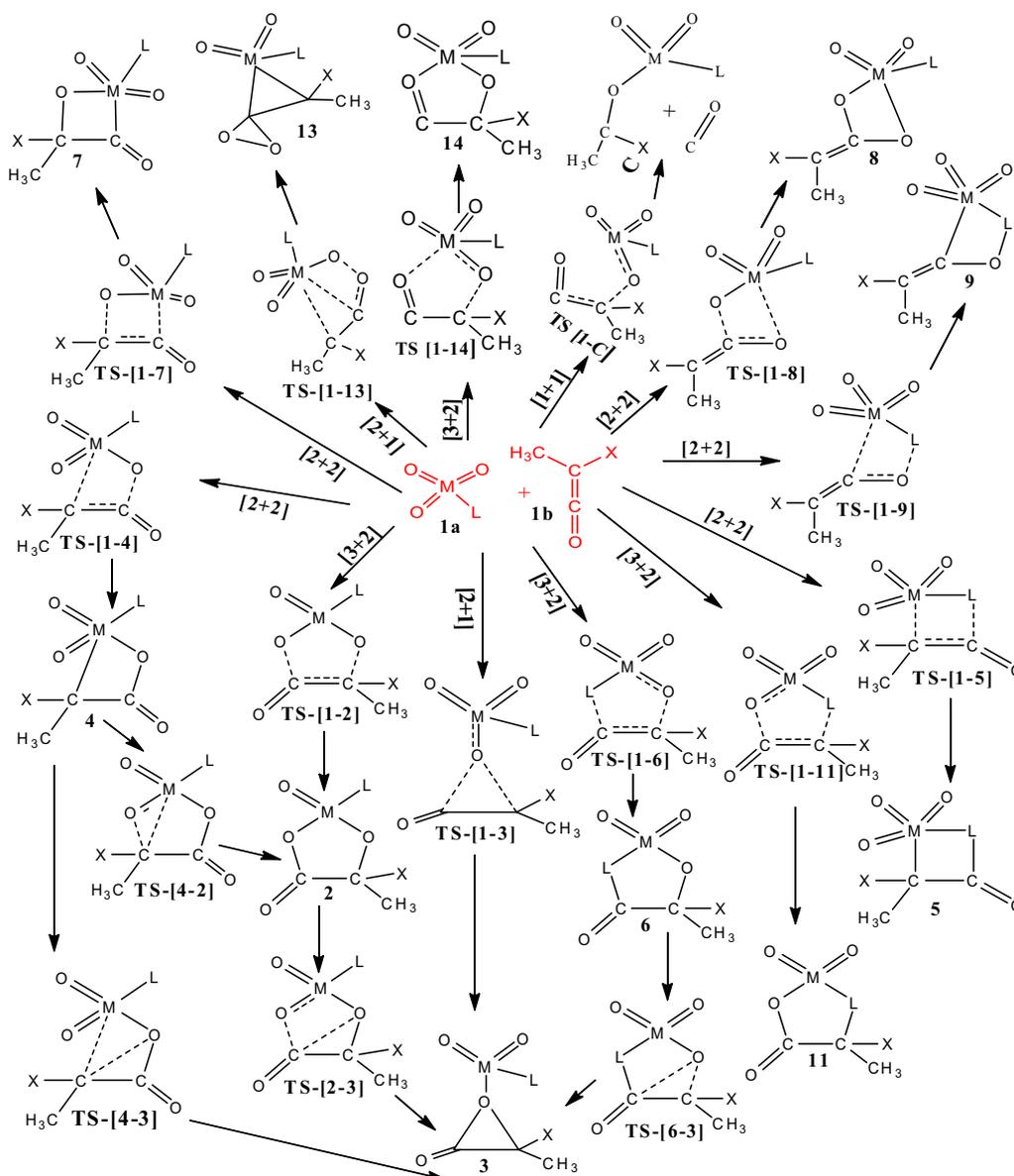
The activation energies involved in the reaction of MnO₃–OCH₃ with dimethyl ketene are relatively lower than those for similar reactions of ReO₃–OCH₃. Also Mn is more selective than Re since there are fewer feasible reaction pathways in MnO₃–OCH₃ than in ReO₃–OCH₃. The chemical reactivity, particularly of the higher homologs, is influenced by the increasing strength of relativistic effects which is in the order Mn < Tc < Re. In the reaction of MO₃–OCH₃ (M = Re, Mn) with dimethyl ketene [2+2] addition

across the C=C was preferred for M = Re but when M = Mn it is [3+2] addition across the C=C of the ketene which is preferred over the [2+2]. This points to the fact that periselectivity also depends on the participating metal of the metal oxide.

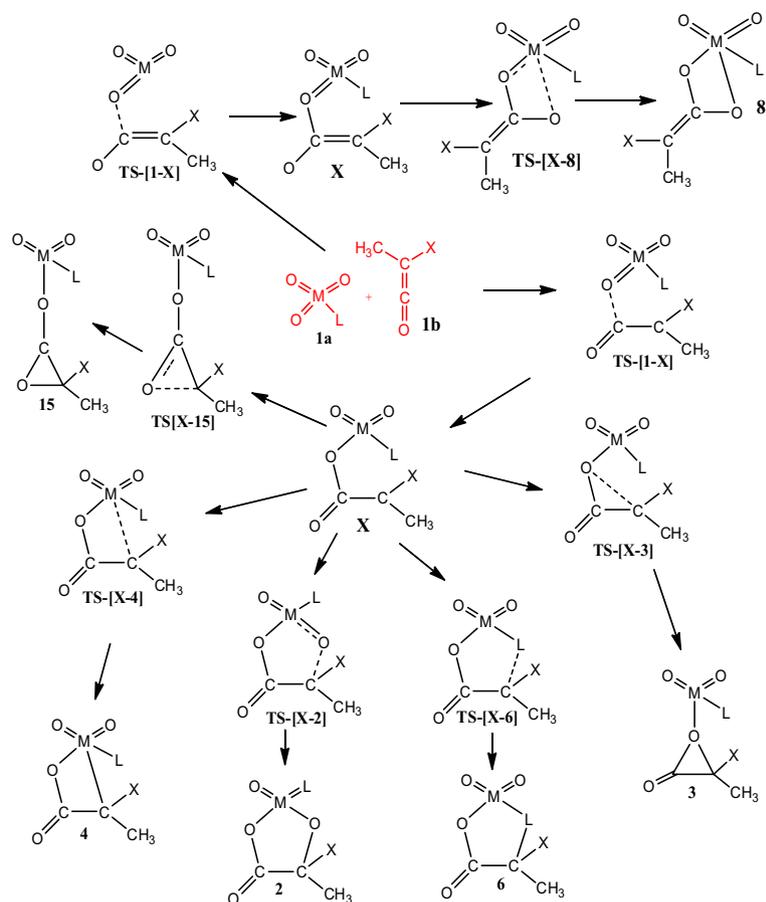
3.1.4. Reaction of MnO₃–CH₃ with dimethyl ketene

Fig. 4 shows the relative energies of the main stationary points involved in the reaction between MnO₃–CH₃ and dimethyl ketene and some of the optimized structures. The energetics are shown in Table 4. The singlet structure of MnO₃–CH₃ is 26.93 kcal/mol more stable than the triplet structure; both species were computed as neutral structures. On the singlet PES, the concerted [3+2] addition of the O=Mn=O bond of the metal oxide across the C=C of the ketene to form species **2** metalla-2,5-dioxolane-4,4-dimethyl-3-one (Fig. 4) has an activation barrier of 8.49 kcal/mol and exothermicity of 57.09 kcal/mol at the B3LYP level of theory through transition state TS-[1-2] and activation barrier of 5.01 kcal/mol and exothermicity 61.46 kcal/mol at the MO6 level.

A stepwise pathway is located towards the formation of the triplet zwitterionic species **X** through transition state TS-[1-X] with



Scheme 1. Proposed pathways for the concerted additions of LMnO₃ (L = O⁻, Cl⁻, CH₃, OCH₃) to substituted ketene and possible re-arrangements.



Scheme 2. Proposed pathways for the stepwise additions of LMnO_3 ($\text{L} = \text{O}^-$, Cl^- , CH_3 , OCH_3) to substituted ketene and possible re-arrangements.

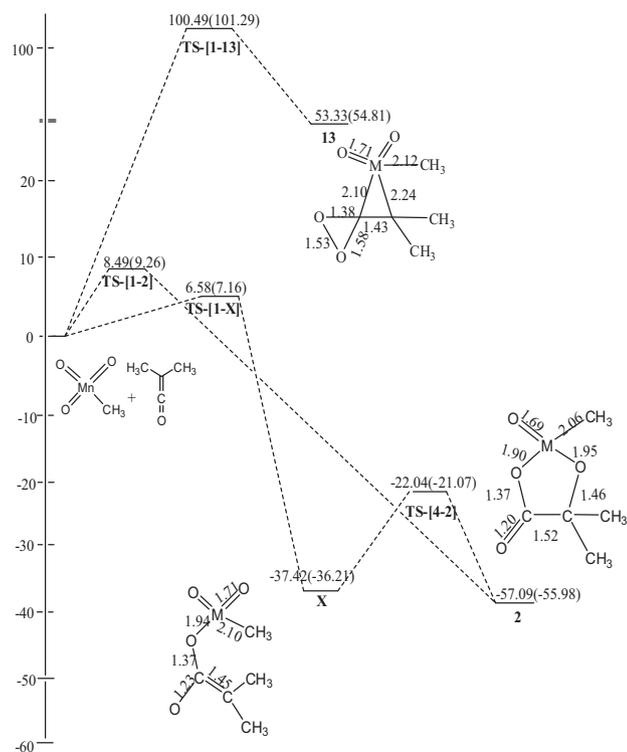


Fig. 4. Energetics of the reaction of $\text{MnO}_3\text{-CH}_3$ with dimethyl ketene on the singlet PES at the B3LYP level of theory. Energies in kcal/mol. Zero-point corrected energies in parentheses.

Table 4

Calculated activation and reaction energies in kcal/mol for the addition pathways in the reaction of $\text{MnO}_3\text{-CH}_3$ with dimethyl ketene at the B3LYP and MO6 levels of theory.

Reaction path	Methyl ligand Addition	Activation energy		Reaction energy	
		B3LYP	MO6	B3LYP	MO6
1 → 2	[3+2] _{C=C}	8.49 (9.26)	5.0 (5.43)	-57.09 (-55.98)	-61.46 (-60.13)
1 → 13	[3+2] _{C=C}	100.49 (101.29)	84.86 (86.12)	53.33 (54.81)	49.29 (50.25)
1 → X	[1+1]	6.58 (7.16)	4.97 (5.02)	-37.42 (-36.21)	-42.12 (-41.13)
X → 2	Re-arrangement	15.38 (15.14)	9.28 (9.89)	-19.67 (-19.77)	-22.58 (-21.27)

Zero-point corrected energies in parentheses.

activation energy 6.58 kcal/mol and reaction energy of -35.78 kcal/mol at the B3LYP level of theory. The singlet zwitterionic species **X** cyclizes through transition state **TS-[X-2]** to form five-membered metallacycle species **2** with activation barrier of 15.38 kcal/mol and exothermicity of 19.67 kcal/mol at the B3LYP level of theory. A direct [1+2] addition of one of the oxygen of the metal oxide across the $\text{C}=\text{O}$ of the ketene leads to the formation of the dioxirane precursor **13** with energy barrier and reaction energy of 100.49 kcal/mol and 53.33 kcal/mol endothermic, respectively at the B3LYP level of theory. The high energy barrier involved in the formation of the dioxirane is due to the change in oxidation number of the metal, from +7 in the reactant (MnO_3Cl)

for the dimethyl ketene (Fig. 1) but an analog (acetaldehyde and carbon monoxide) was located for the methyl ketene system (Fig. 5). No [2+2] addition pathway is located on this potential energy surface just as in the case for all the Mn-metal catalyst systems with the ketenes.

The most plausible addition pathway on this PES is the concerted [3+2] addition of the Mn=O bond of the metal oxide across the C=C=O of the ketene to form acid chloride precursor and carbon monoxide species **C**. There is not much difference in the selectivity of this reaction compared to the dimethyl ketene system, however, three plausible elementary steps are seen for this system against three plausible elementary steps for the dimethyl system. Therefore replacing a dimethyl ketene with chloro methyl ketene does not affect the selectivity but raises the energy slightly for the formation of similar analog species but does not really affect the reactivity.

This system (chloro methyl ketene reaction surface with the MnO₃Cl) is potentially more selective compared to the methyl ketene systems but comparatively same as the dimethyl ketene.

3.2.3. Reaction of MnO₃Cl with cyano methyl ketene

As in the case of the dimethyl ketene, methyl ketene and chloro methyl ketene, no [2+2] addition pathway is located towards the formation of the four-membered metallacycle intermediate. However, replacing the dimethyl ketene with cyano methyl ketene, a

decrease in activation barrier of about 2.57 kcal/mol is noted in the formation of the species **2** with a respective decrease in exothermicity of about 3.05 kcal/mol. The formation of the triplet zwitterionic intermediate **X/t** also sees a 4.12 kcal/mol increase in activation barrier and a change in reaction energy from –40.44 kcal/mol to –38.53 kcal/mol, respectively. The triplet zwitterionic intermediate **X/t** then cyclizes to form species **15/s** with energy barrier of 39.95 kcal/mol and reaction energies of 33.70 kcal/mol.

The formation of the carbon monoxide and carbonyl group precursor species **C/s** is no longer viable for the cyano methyl ketene system just in the case of the dimethyl ketene. These reactions seem possible only in the MnO₃Cl–chloro methyl ketene and MnO₃Cl–methyl ketene cases. The formation of the dioxirane precursor **13** (Fig. S3 in the electronic supporting information) just as in the case of the chloro methyl ketene has activation barrier of 105.29 kcal/mol and endothermicity of 52.07 kcal/mol this reaction looks highly unlikely. This step is not seen in the dimethyl ketene and methyl ketene systems. It is seen that the formation of species **6**, is no longer feasible due to the presence of a more electronegative substituent (CN) compared to the methyl group.

The most plausible addition pathway on this PES is the concerted [3+2] addition of the O=Mn=O bond of the metal oxide across the C=C bonds of the ketene to form the species **2**.

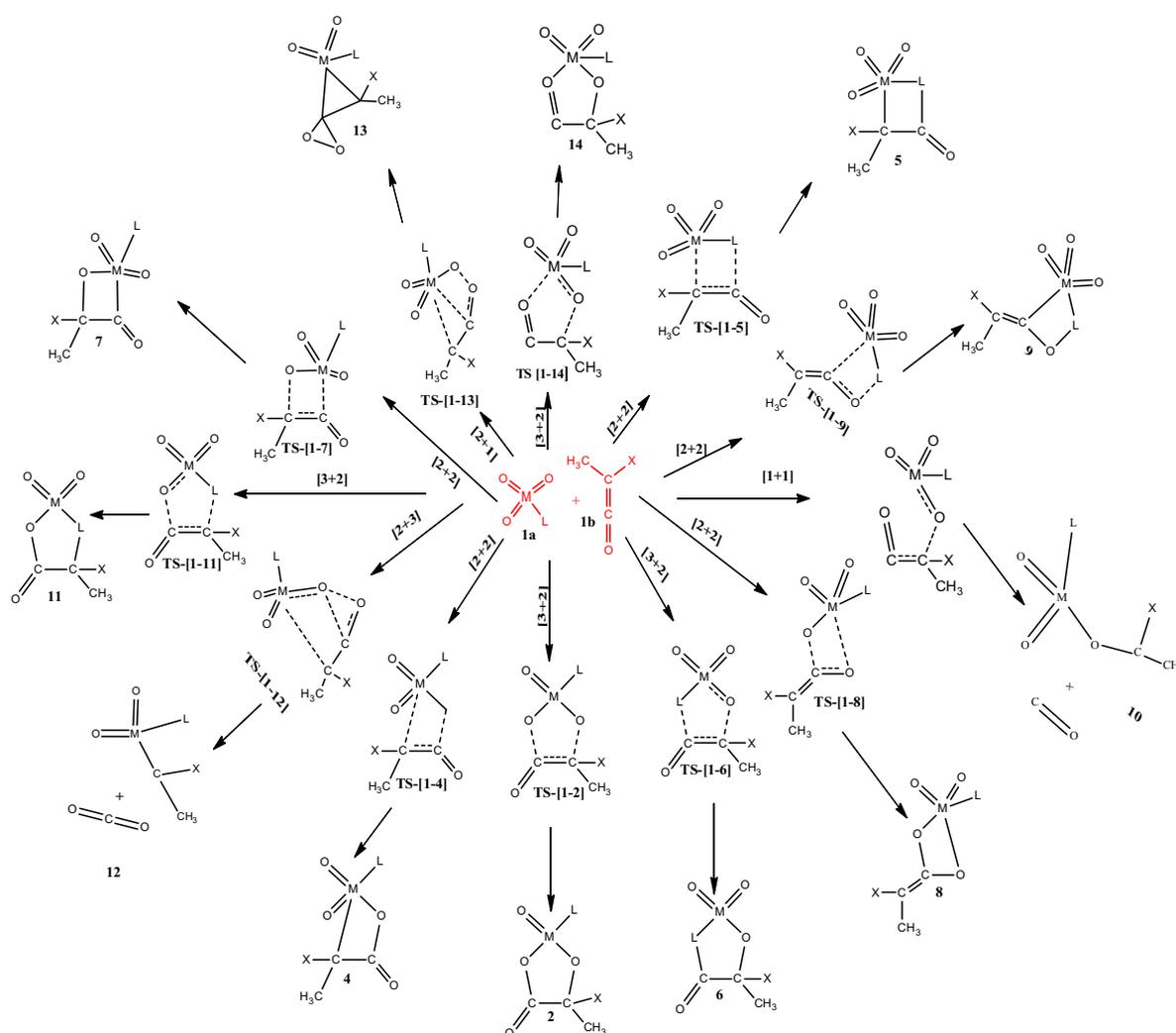


Fig. 5. Summary of possible reaction paths for the reaction of MO₃L (M = Re^c, Mn; L = Cl⁻, O⁻, OCH₃, CH₃) with ketenes.

Table 6
Comparison of the peri-, chemo-, and regio-selectivity of the reactions of Mn and Re: activation barriers and reaction energies for the first step of the various reactions of the Mn and Re complexes with dimethyl ketene.

Metal	Reaction path	Addition	Activation barriers			Reaction energies					
			-Cl	-O ⁻	OCH ₃	CH ₃	-Cl	-O ⁻	OCH ₃	CH ₃	
Mn	1-2	[3+2] _{C=C}	6.01 (6.48)	-	7.74 (8.04)	8.49 (9.02)	-68.09 (-67.42)	-	-76.18 (-75.04)	-57.09 (-56.42)	
	1-6	[3+2] _{C=C}	1.12 (1.29)	-	4.24 (4.99)	-	-33.53 (-33.03)	-	-60.93 (-57.92)	-	
	1-4	[2+2] _{C=C}	-	-	-	-	-	-	-	-	
	1-8	[2+2] _{C=C}	-	-	-	-	-	-	-	-	
	1-9	[2+2] _{C=O}	-	-	22.38 (23.79)	-	-	-	-16.84 (-14.08)	-	
	1-11	[3+2] _{C=C}	-	-	-	-	-	-	-	-	
	1-14	[3+2] _{C=C=O}	-	-	-	-	-	-	-	-	
	1-X	[1+1]	0.94 (0.99)	-0.83 (0.24)	-	6.58 (7.12)	-40.44 (-39.76)	-9.35 (-9.01)	-	-37.42 (-36.85)	
	Re ^a	1-2	[3+2] _{C=C}	22.59 (23.08)	20.16 (20.68)	24.79 (25.14)	33.95 (33.92)	-16.95 (-13.81)	-17.43 (-14.50)	-16.16 (-12.91)	-1.20 (1.25)
		1-6	[3+2] _{C=C}	-	-	24.13 (24.73)	-	1.31 (3.72)	-	-6.59 (-3.18)	-
1-4		[2+2] _{C=C}	13.64 (14.62)	12.54 (11.83)	41.69 (42.79)	20.71 (21.82)	-8.22 (-6.12)	-12.13 (-10.67)	-17.35 (-14.69)	-15.43 (-12.62)	
1-8		[2+2] _{C=O}	18.68 (19.05)	6.40 (6.53)	17.87 (18.26)	18.38 (18.81)	-6.14 (-4.60)	-8.36 (-6.60)	-3.46 (-1.56)	-6.99 (-5.03)	
1-9		[2+2] _{C=O}	19.10 (19.82)	-	18.08 (19.17)	50.00 (50.31)	-12.79 (-11.18)	-	-12.22 (-9.88)	-26.78 (-24.01)	
1-11		[3+2] _{C=C}	24.07 (24.78)	-	-	-	-	-	-	-	
1-14		[3+2] _{C=C=O}	21.48 (21.88)	-	-	24.18 (25.08)	12.93 (13.43)	-	-	15.74 (16.01)	
1-X		[1+1]	17.94 (17.77)	-	22.39 (21.18)	18.08 (18.19)	0.23 (0.77)	-	3.93 (4.45)	1.98 (2.58)	

Zero-point corrected energies in parentheses.

^a Data from Ref. [4].

This reaction has energy barriers similar to those for the dimethyl ketene, methyl ketene and chloro methyl ketene system for the identified species. However, this system has fewer feasible reaction pathways on the singlet PES than the dimethyl ketene, methyl ketene and chloro methyl ketene. This makes the cyano methyl ketene reaction surface with the metal catalyst (MnO₃Cl) more selective compared to the three other ketene systems discussed previously even though they are all selective.

3.2.4. Reaction of MnO₃Cl with methyl phenyl ketene

The activation and reactions energies involved in the reaction between MnO₃Cl and methyl phenyl ketene is also captured in Table 5 and Fig. S4 (in electronic supporting information) shows the optimized geometries and relative energies of the main stationary points involved in the reaction between MnO₃Cl and methyl phenyl ketene. It is realized that the formation of the phenyl analog of species **2** by replacing one of the methyl groups on the ketene (dimethyl ketene) with a phenyl group (methyl phenyl ketene) leads to the raising of the activation energy by 0.05 kcal/mol but decreases the reaction energy by 8.97 kcal/mol. It is also seen an increase in the activation barrier of about 2.21 kcal/mol in the formation of the triplet zwitterionic intermediate **X/t** with the reaction energy changing from -40.44 kcal/mol to -31.47 kcal/mol. The triplet zwitterionic intermediate **X/t** then cyclizes to form species **8/s** with energy barrier of 11.01 kcal/mol and exothermicity of -36.78 kcal/mol.

The most plausible addition pathway on this PES is the concerted [3+2] addition of the O=Mn=O bond of the metal oxide across the C=C of the ketene to form species **2** intermediate. There are no local minima corresponding to intermediates **4** and **6**; this is attributed to the presence of bulkier and more electronegative substituent (Ph) compared to the methyl group. The methyl phenyl system has energy barriers similar to those for the dimethyl ketene, methyl ketene and chloro methyl ketene system for the identified species. However, this system has fewer feasible reaction pathways on the singlet PES than the dimethyl ketene, methyl ketene, chloro methyl and cyano methyl ketene. This makes the methyl phenyl ketene reaction surface with the metal catalyst (MnO₃Cl) the most selective compared to all the other ketene systems discussed previously.

3.3. Comparison of the reaction of MnO₃L with ReO₃L with substituted ketenes

The activation barriers and reaction energies for the first step of the various reactions of MnO₃L and ReO₃L with ketene for the various ligands studied in this work and in our earlier reported work on Re⁴ is shown in Table 6. It is seen from the table that for all the ligands O⁻, CH₃, OCH₃, Cl⁻, the [3+2] pathway is the most preferred pathway for the Mn complexes whiles the [2+2] pathway is the most preferred pathway for the Re complexes. The activation barriers for the formation of similar analogs are lower for the Mn complexes than for the Re complexes and reaction energies for Mn are more exothermic than those for Re. A similar trend in activation barriers was observed in Aniagyei [7–9] involving group VII transition metal oxides with alkene.

It is also seen from the table that the reactions of the Mn complexes are more selective than the reactions of the Re complexes, since there are fewer competitive reaction pathways with the Mn complexes than with the Re complexes. A similar trend was also seen in Aniagyei et al. [7–9] for the reactions of group VII transition metal oxides with ethylene.

These results imply that manganese oxo complexes efficiently and selectively catalyze specific reactions in oxidation of ketenes and olefins than do Re oxo complexes. Therefore Mn oxo

complexes may be better catalysts for specific oxidation reactions of ketenes and olefins than Re complexes are.

4. Summary and conclusions

1. The periselectivity in the reactions of metal oxides (MnO_3L) with substituted ketenes depends on the metal of the catalyst (MnO_3L). The concerted [3+2] addition of the C=C bond of the ketene across the metal complex is the most preferred pathway in all the reactions studied except in the reaction of MnO_4^- with dimethyl ketene, which follows only a stepwise addition pathway. [2+2] addition is found to be possible only in the reaction of $\text{MnO}_3\text{-OCH}_3$ (i.e. $\text{L} = \text{OCH}_3$) with dimethyl ketene where the activation barrier for [2+2]_{C=O} addition is 23.79 kcal/mol, which is far greater than the barrier for the [3+2] addition.
2. Chemoselectivity (C=C – versus – C=O) of the [2+2] addition of MnO_3L also depends on the Ligand L. The only [2+2] addition pathway that has been found (i.e. in $\text{L} = \text{OCH}_3$) is a [2+2]_{C=O} and not [2+2]_{C=C} addition. Thus [2+2]_{C=C} is precluded in all the reactions studied.
3. The order in the activation energies of the preferred [3+2] and [2+2] pathways for addition of dimethyl ketenes to the metal complexes MnO_3L with respect to changing ligand L is $\text{O}^- < \text{Cl} < \text{CH}_3 < \text{CH}_3\text{O}^-$ while the order in reaction energies is $\text{CH}_3 < \text{CH}_3\text{O}^- < \text{Cl} < \text{O}^-$. For the reactions of substituted ketenes with MnO_3Cl , the order in activation barriers for the preferred addition pathways is $\text{Cl} < \text{H} < \text{CN} < \text{CH}_3 < \text{Ph}$ while the reactions energies follow the order $\text{H} < \text{CH}_3 < \text{CN} < \text{Ph} < \text{Cl}$.
4. In the reactions of dimethyl ketenes with MnO_3L , the trend in the selectivity of the reactions is $\text{Cl}^- < \text{CH}_3\text{O}^- < \text{CH}_3 < \text{O}^-$ while the trend in selectivity is $\text{H} < \text{Cl} < \text{CH}_3 < \text{CN} < \text{Ph}$ in the reactions of MnO_3Cl with substituted ketenes ($\text{O}=\text{C}=\text{C}(\text{CH}_3)(\text{X})$; $\text{X} = \text{H}, \text{CH}_3, \text{Cl}, \text{CN}, \text{Ph}$).
5. Reactions involving an increase in oxidation state of metal have high activation barriers while reactions that do not involve a change in oxidation state have low activation barriers. The changes in oxidation state were observed for substituents or ligands with electron-withdrawing or donating inductive effect. This agrees with the work of Ahmed et al. [4].
6. For these addition reactions studied, low activation barriers are obtained when the substituent on the ketene is electron-donating while high activation barriers are obtained when the substituent is electron withdrawing. This is consistent with Re oxides work reported earlier [4].
7. The reactions of ketenes with MnO_3L complexes have lower activation barriers for the preferred [3+2] and [2+2] addition pathways as well as fewer side reactions than those of the ReO_3L complexes reported in the literature, a trend which was seen in our earlier work with reactions of group VII metals with olefins, implying that manganese oxo complexes efficiently and

selectively catalyze specific reactions in oxidation of ketenes and olefins than do Re oxo complexes and therefore Mn oxo complexes may be better catalysts for specific oxidation reactions of ketenes and olefins than Re complexes are.

Competing interests

The authors declare that they have no competing interests whatsoever.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2015.11.006>.

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