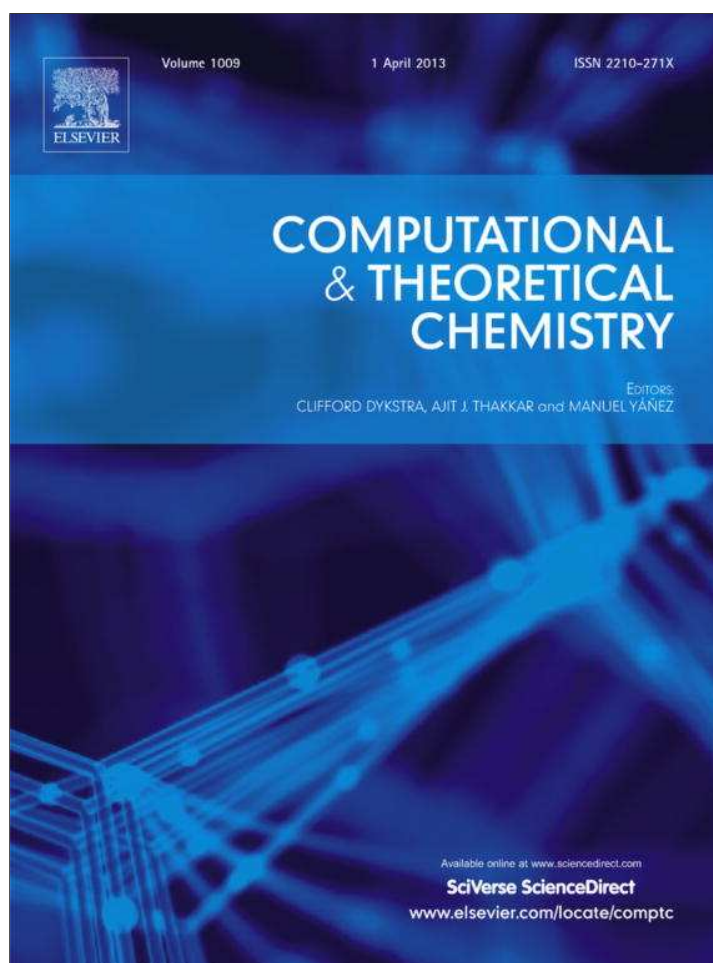


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A density functional theory study of the mechanisms of oxidation of ethylene by technetium oxo complexes

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ABSTRACT

The mechanisms of oxidation of ethylene by transition metal-oxo complexes of the type $LTcO_3$ ($L = O^-, Cl, CH_3, OCH_3, Cp, NPH_3$) have been explored by computing the activation barriers and reaction energies for the concerted and stepwise addition pathways at the density functional theory B3LYP/LACVP* level of theory. The results indicate that in the reaction of $LTcO_3$ ($L = O^-, Cl, CH_3, OCH_3, Cp, NPH_3$) with ethylene, the formation of the dioxylate intermediate through the concerted [3 + 2] addition pathway on the singlet potential energy surface is favored kinetically and thermodynamically over its formation through the two-step process via the metallaoxetane intermediate. The activation barrier for the formation of the dioxylate on the singlet PES for the ligands studied is found to follow the order: $O^- > CH_3 > NPH_3 > CH_3O^- > Cl^- > Cp$ while the reaction energies follow the order: $Cl^- > O^- > CH_3 > NPH_3 > CH_3O^- > Cp$. On the doublet PES, the [2 + 2] addition leading to the formation of the four-membered metallacycle intermediate is favored kinetically and thermodynamically for the ligands when $L = NPH_3$. The direct [2 + 1] addition of ethylene across the oxo- ligand of doublet $TcO_3(CH_3)$ to form the epoxide precursor is favored when $L = CH_3$. The activation barriers for the formation of the dioxylate intermediate are found to follow the order: $Cl^- < CH_3O^- < CH_3$ while the reaction energies follow the order $Cl^- < CH_3O^- < CH_3$. The rearrangement of the metallaoxetane intermediate to the dioxylate is not a feasible pathway for the formation of the dioxylate. The formation of the epoxide precursor will not result from the reaction of $LTcO_3$ ($L = O^-, Cp$) with ethylene on all the surfaces explored. There does not appear to be a spin-crossover in any of the pathways studied.

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1. Introduction

The development of new catalytic reactions that perform chemical transformations with high selectivity and efficiency is a key objective in chemical research. Many new reactions are discovered serendipitously, but increasing mechanistic knowledge permits the rational design of new reactions of key intermediates. Although enormous efforts have been made to find out experimentally the mechanism of transition-metal catalyzed processes, most reactions are still little understood in terms of mechanistic details [1–4].

Transition-metal-complex-mediated oxygen-transfer reactions are of considerable importance in chemistry, both in the industrial arena and under laboratory conditions. The addition of osmium tetroxide across the C=C double bond of olefins yielding a metalla-2,5-dioxolane is the initial step of *cis*-dihydroxylation, one of the most elegant reactions for a 1,2-functionalization of alkenes [5–7]. Some transition metal-oxo complexes such as CrO_2Cl_2 [8–10] react with olefins to form epoxides, chlorohydrins and

vicinal dihalides whereas others such as MnO_4^- and OsO_4^- react to form diols without significant epoxide formation [11,12].

The oxo complexes of group VII (Mn, Tc, and Re) are of great interest for their tendency toward epoxidation and dihydroxylation. MnO_4^- is commonly used as a dihydroxylation agent [13] while the system CH_3ReO_3/H_2O_2 is experimentally known to be an efficient epoxidation catalyst [14–18]. With allusion to these two types of oxidation reactions, Tc is intermediate [19]. Electronic and structural properties of Mn [20], Tc [19] and Re [17,18] compounds have previously been analyzed in various density functional theory studies. Differences in reactivity between analogous Tc and Re oxo compounds have been attributed to relativistic effects on the Lewis acidity and the polarizability of the MO_3 moiety. Re was found to form a stronger and harder (less polarizable) Lewis acid center than Tc [16–18]. $CpReO_3$ [21–24] has been shown to react with olefins to predominately form dioxylates.

Gisdakis and Rösch [25] in a theoretical study of ethylene addition to $LTcO_3$ ($L = Cp, Cl, CH_3$ and O^-) calculated the [3 + 2] addition pathway leading to the dioxylate to have a lower activation barrier than the corresponding [2 + 2] addition pathway leading to the formation of the metallaoxetane. Haunschild and Frenking [26] calculated the [2 + 2] addition pathway to be favored when a transition

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metal–carbon double bond is present. For ethylene addition to $\text{TcO}_2(\text{CH}_3)(\text{CH}_2)$, the [2 + 2] addition across the $\text{Tc}=\text{CH}_2$ becomes more favorable than the [3 + 2] addition pathway across the two oxygen atoms and oxygen and carbon atoms of $\text{TcO}_2(\text{CH}_3)(\text{CH}_2)$.

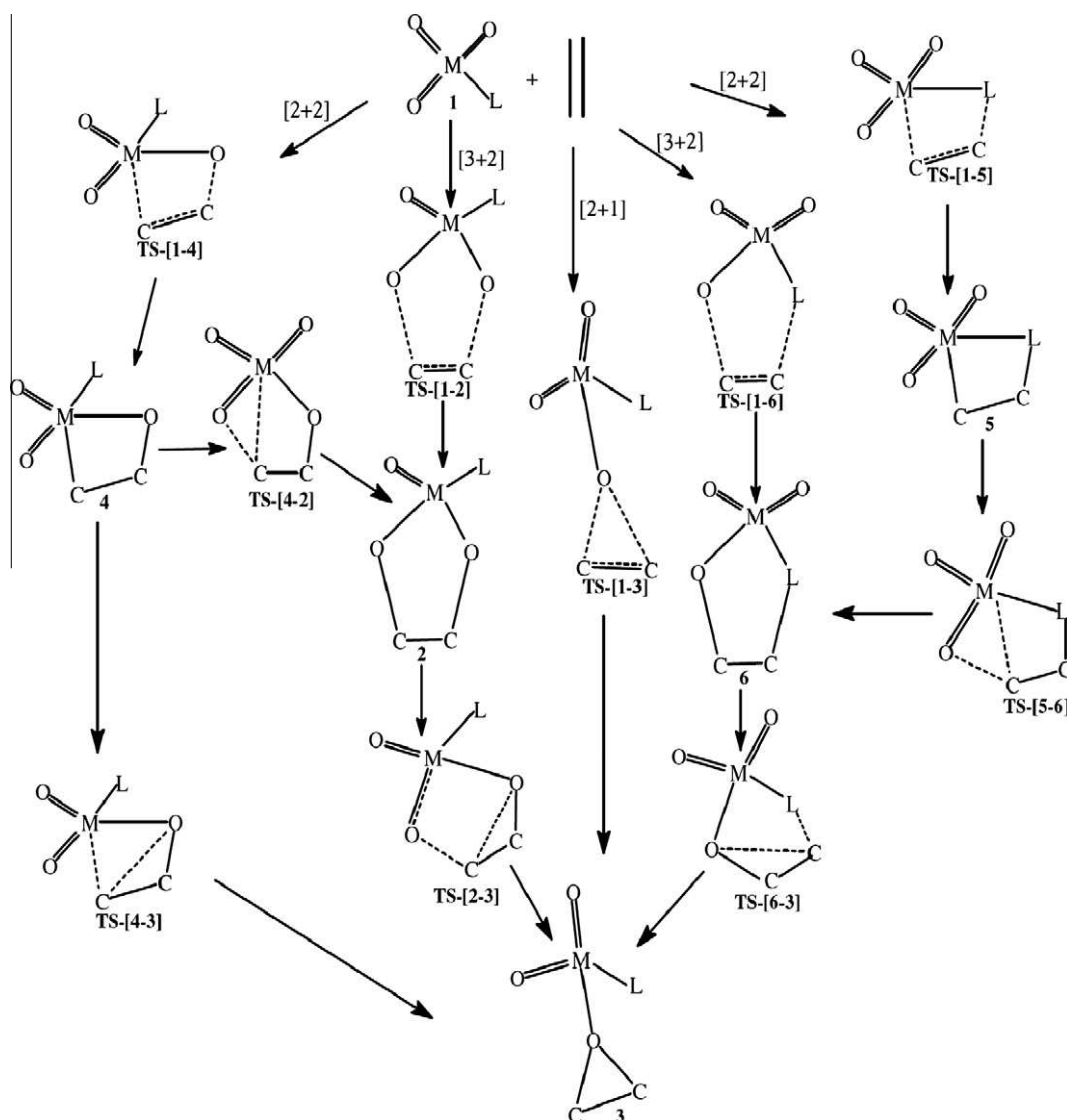
The aim of this work is to extend the work of Gisdakis and Rösch [25] by employing hybrid density functional theory calculations at the B3LYP/LACVP* level of theory to explore several [3 + 2] and [2 + 2] addition pathways for the oxidation of ethylene by LTcO_3 ($\text{L} = \text{O}^-$, Cl , Cp , CH_3 , OCH_3 , NPH_3) and to investigate the possible mechanistic channels for the formation of an epoxide precursor (Schemes 1 and 2). Multiple spin states have been considered in the calculations. Organometallic reactions are known to occur on more than spin surface [27]; many reactions involve several states of different spin [28]. A change of spin state can affect the molecular structure in terms of bond lengths, angular distortions and even overall molecular geometry [29] and spin crossing effects can dramatically affect reaction mechanisms of organometallic transformations [30].

2. Details of calculation

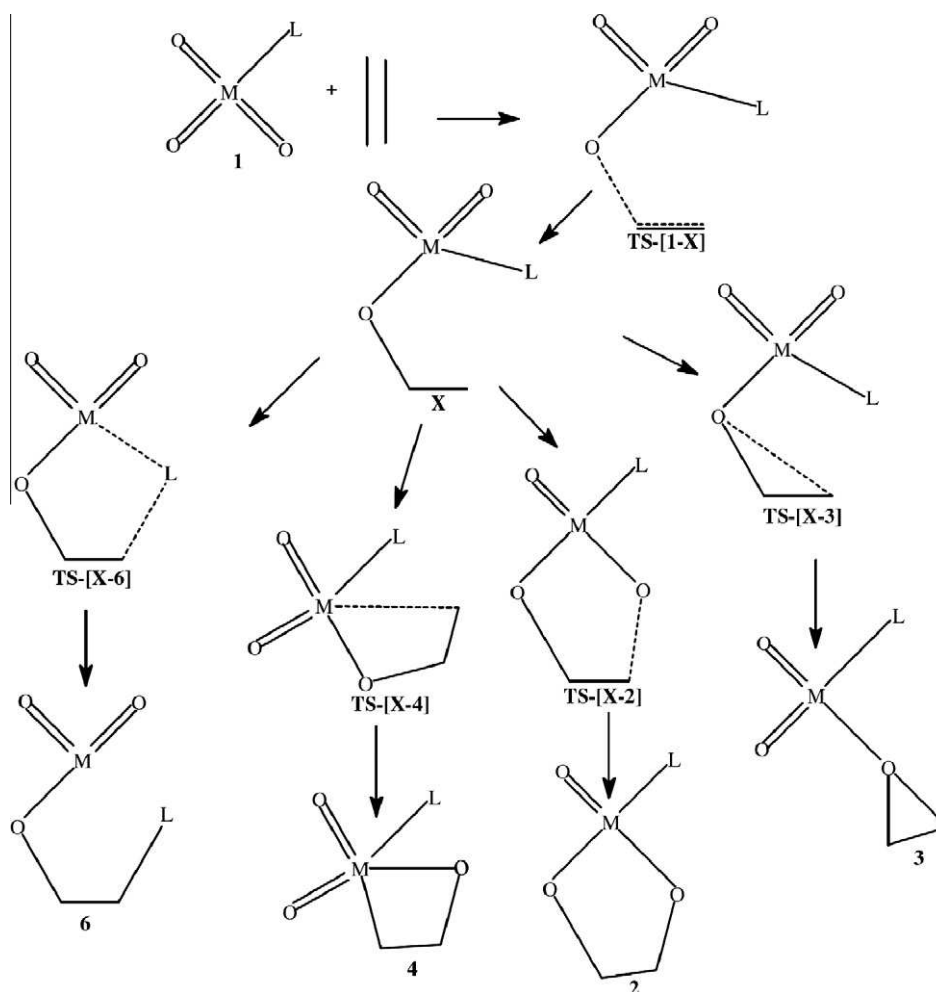
All calculation were carried out with the Spartan '08 V1.2.0 and '10 V1.1.0 Molecular Modeling programs [31] at the DFT B3LYP/

LACVP* level of theory. The B3LYP is an HF-DFT hybrid functional. The LACVP* basis set is a relativistic effective core potential that describes the atoms H–Ar with the 6-31G* basis while heavier atoms are modeled with the LanL2DZ basis set which uses the all-electron valence double zeta basis set (D95V), developed by Dunning, for first row elements [32] and the Los Alamos ECP plus double zeta basis set developed by Wadt and Hay for the atoms Na–La, Hf–Bi [33–35].

The starting geometries of the molecular systems were constructed using Spartan's graphical model builder and minimized interactively using the sybyl force field [36]. All geometries were fully optimized without any symmetry constraints. A normal mode analysis was carried out to verify the nature of the stationary points. Equilibrium geometries were characterized by the absence of imaginary frequencies. The transition state structures were located by a series of constrained geometry optimization in which the forming- and breaking-bonds were fixed at various lengths while the remaining internal co-ordinates were 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 points were shown to have a Hessian matrix with a single negative eigenvalue, characterized by an imaginary vibrational frequency along the reaction coordinate.



Scheme 1. Proposed concerted pathway for the reaction of LMO_3 ($\text{M} = \text{Tc}$ and $\text{L} = \text{O}^-$, Cl^- , NPH_3 , CH_3 , OCH_3 , Cp) with ethylene.



Scheme 2. Proposed stepwise pathway for the reaction of LMO_3 ($M = Tc$, $L = O^-, Cl^-, CH_3O^-, CH_3, Cp, NPH_3$) with ethylene.

For the TcO_3Cl , $TcO_3(CH_3)$, $TcO_3(OCH_3)$, TcO_3Cp and $TcO_3(NPH_3)$ systems, the singlet and triplet species were computed as neutral structures while the doublet and quartet species were computed as anions. For the TcO_4^- system the singlet and triplet species were computed as anions while the doublet and quartet species were computed as neutral structures.

3. Results and discussion

3.1. Reaction of TcO_4^- with ethylene

Fig. 1 shows the energy profile of the reaction of between TcO_4^- and ethylene as well as some of the optimized structures of the main stationary points (reactants, transition states, intermediates and products) involved in the reaction. (The full set of optimized structures for all the systems herein reported is shown in Figs. S1–S6 in the Supporting information attached.) The TcO_4^- reactant has been found to have singlet and triplet ground state electronic states but the singlet is 117 kcal/mol more stable than the triplet. The neutral form of the reactant (TcO_4) has a doublet ground state electronic structure.

On the singlet surface, the direct [3 + 2] addition of the C=C π bond of ethylene across the O=Tc=O bonds of TcO_4^- to form the dioxylate has an activation barrier of 24.22 kcal/mol and reaction energy of -9.46 kcal/mol. The triplet dioxylate species is 48.54 kcal/mol less stable than the singlet. Gisdakis and Rösch [25] computed the barrier along this route to be 27.30 kcal/mol

at the hybrid B3LYP level with the LanL2DZ basis set for the transition metals and 6-311G(d,p) basis set for H, C, O, and F. The neutral form of the dioxylate exhibits doublet and quartet spin states. The quartet state is 51.32 kcal/mol more stable than the doublet state. The formation of the singlet metallaoxetane through the singlet transition state by [2 + 2] addition of the C=C bond of ethylene across the Tc=O bond of the pertechnetate reactant has an activation barrier of 48.20 kcal/mol and reaction energy of 17.40 kcal/mol. A triplet metallaoxetane has been found to be 33.98 kcal/mol more stable than the singlet.

The re-arrangement of the metallaoxetane to the dioxylate (i.e. TS-[4-2] in Scheme 1) as suggested by Sharpless et al. [37] in the chromyl chloride oxidation of olefins was explored for the reaction of TcO_4^- with ethylene. The re-arrangement of the singlet metallaoxetane through a singlet transition state to the singlet dioxylate has an activation barrier of 56.53 kcal/mol (Fig. 1) while a re-arrangement of the triplet metallaoxetane through a singlet transition state to the singlet dioxylate has a barrier of 22.55 kcal/mol. Thus, the overall barrier for the re-arrangement of the metallaoxetane to the dioxylate is higher than the activation barrier for the direct [3 + 2] addition across the two oxygen atoms of TcO_4^- . This rules out the two-step process for the formation of dioxylate from the metallaoxetane and therefore the dioxylate intermediate would be formed from the direct [3 + 2] addition of ethylene across the O=Tc=O bond of singlet TcO_4^- .

The potential energy surface of the reaction of TcO_4^- with ethylene was further explored in an attempt to locate an epoxide

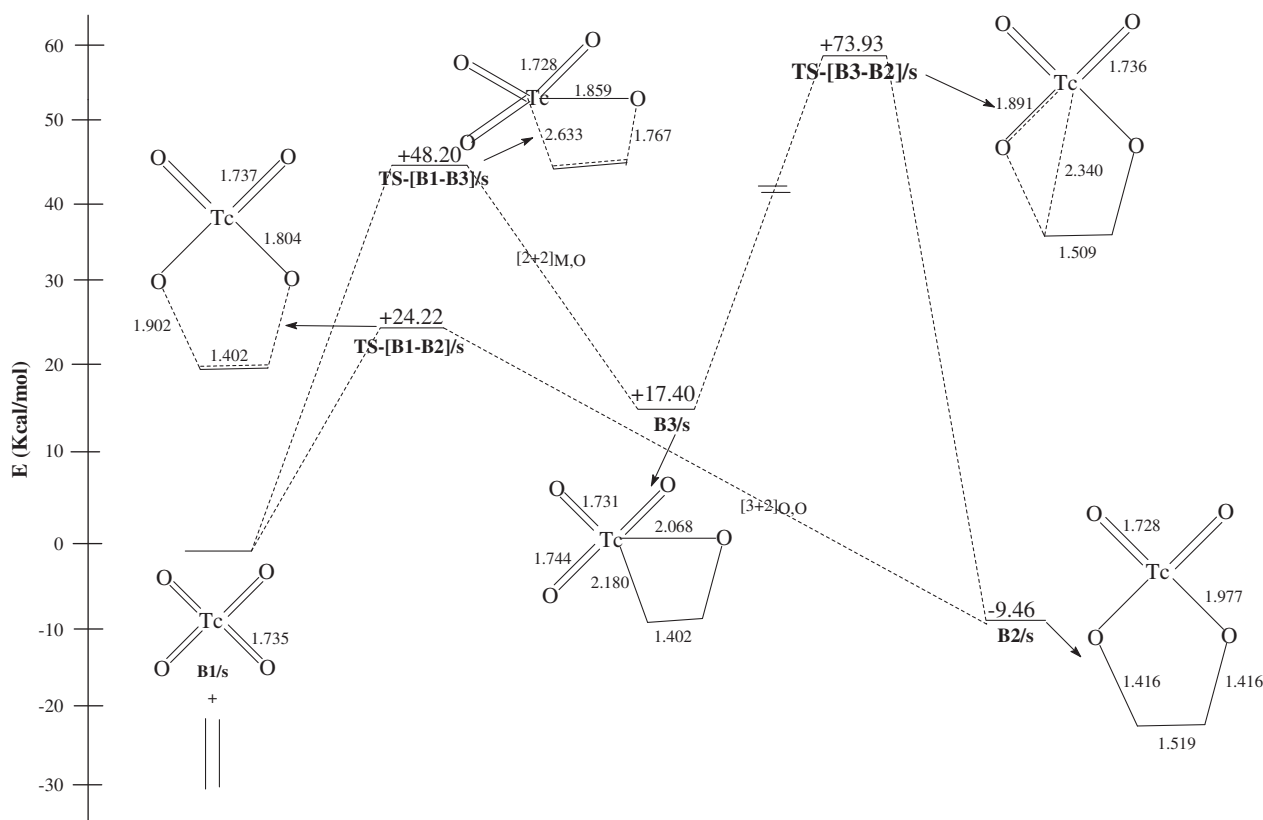


Fig. 1. Energetics of the reactions of TcO_4^- with ethylene. Relative energies in kcal/mol.

precursor ($\text{O}_3\text{--Tc--OC}_2\text{H}_4$) (structure **3** in Scheme 1), but no such minimum was found on these reaction surfaces.

3.2. Reaction of TcO_3Cl with ethylene

The energy profile of the reaction between TcO_3Cl and ethylene and some of the optimized structures involved in the reaction are shown in Fig. 2. The singlet reactant is 111.26 kcal/mol more stable than the triplet reactant while the doublet reactant is 58.88 kcal/mol more stable than the quartet reactant.

On the singlet surface, the [3 + 2] addition of the C=C bond of ethylene across the O=Tc=O bonds of TcO_3Cl to form the dioxyate has an activation barrier of 7.57 kcal/mol and reaction energy of -28.13 kcal/mol, which is in agreement with the activation barrier and reaction energy reported by Kühn et al. [24] at the hybrid B3LYP level with the LanL2DZ basis set for the transition metals and 6-311G(d,p) basis sets for H, C, O, and F.

On the doublet surface, the [3 + 2] addition of C=C bond of ethylene across the O=Tc=O functionality of TcO_3Cl could follow either the stepwise or concerted pathways. On the concerted pathway, the addition across the two oxygen atoms of TcO_3Cl to form the dioxyate has an activation barrier of 20.18 kcal/mol and reaction energy of -17.22 kcal/mol.

On the stepwise pathway, the C=C π of ethylene attacks one oxygen atom of TcO_3Cl to form the organometallic intermediate (structure **X** in Scheme 2) through transition state. This first step has an activation barrier of 30.38 kcal/mol and reaction energy of +24.67 kcal/mol. The intermediate then re-arranges in a barrierless step to form the dioxyate intermediate, with a reaction energy of -41.89 kcal/mol.

No triplet or quartet transition states could be located for the formation of the dioxyates but triplet and quartet dioxyates were found. The triplet dioxyate is 44.73 kcal/mol more stable than the

singlet while the quartet dioxyate is 36.14 kcal/mol more stable than the doublet.

On the singlet pathway, the direct [3 + 2] addition of the C=C bond of ethylene across the O=Tc=Cl functionality of singlet TcO_3Cl has activation barrier of 14.67 and a reaction energy of -1.70 kcal/mol.

The formation of the singlet metallaoxetane through a singlet transition state has an activation barrier of 32.07 kcal/mol and reaction energy of +0.41 kcal/mol. The formation of doublet metallaoxetane through the doublet transition state by [2 + 2] addition of the C=C bond of ethylene across Tc=O bond of the TcO_3Cl complex has an activation barrier of 29.12 kcal/mol and the metallaoxetane intermediate has reaction energy of -6.53 kcal/mol. The barrier for this step is only 1.26 kcal/mol higher than the barrier for the formation of the organometallic intermediate **X/d** (vide supra); this might lead to a competition between the two reactions. Attempts at forming the metallaoxetane intermediate from the stepwise pathway proved unsuccessful. This indicates that metallaoxetane intermediate is formed from the concerted pathway and not the stepwise route. A triplet metallaoxetane has been computed to be 33.71 kcal/mol more stable than the singlet metallaoxetane. No triplet or quartet [2 + 2] transition states connecting the reactants to the products could be located on the reaction surface explored.

The re-arrangement of the singlet, doublet, triplet and quartet metallaoxetane to the five-membered dioxyate (i.e. **TS-[4-2]** in Scheme 1) was explored for the reaction of TcO_3Cl with ethylene. The re-arrangement of the singlet metallaoxetane to the singlet dioxyate through the singlet transition state has an activation barrier of 27.83 kcal/mol. On the doublet surface, the activation barrier is 42.49 kcal/mol. No transition state was located for the re-arrangement of the metallaoxetane to the dioxyate on the triplet and quartet surfaces.

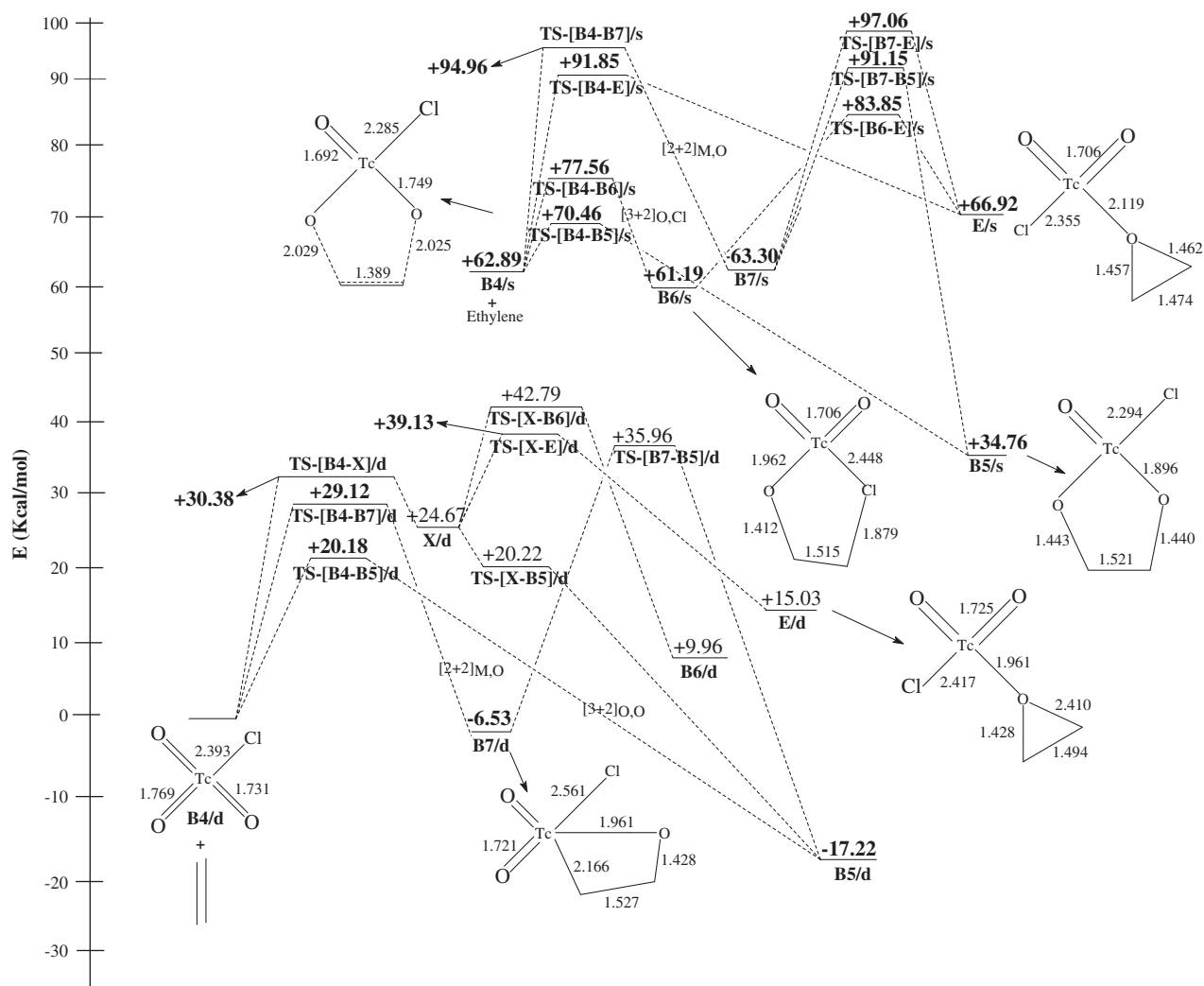


Fig. 2. Energetics of the reactions of TcO_3Cl with ethylene (s = singlet, d = doublet). (Note that the singlet structures and the doublet structures are not isoelectronic and therefore their energies are not to be compared directly.)

The activation barriers (26.75 and 42.49 kcal/mol) for the re-arrangement of the singlet and doublet metallaoyxetane to the dioxylyate are higher than the activation barrier for the direct [3 + 2] addition across the two oxygen atoms of singlet and doublet TcO_3Cl . This means the formation of the dioxylyate on both the singlet and doublet surfaces will proceed from the direct [3 + 2] addition of ethylene across the $\text{O}=\text{Tc}=\text{O}$ bonds of singlet and doublet TcO_3Cl .

An epoxide precursor formation was explored for the reaction of TcO_3Cl with ethylene. The re-arrangement of the singlet five-membered metallacycle **B6/s** to the epoxide precursor has an activation barrier of 22.66 kcal/mol and reaction energy of +5.73 kcal/mol while the re-arrangement of the singlet four-membered metallaoyxetane **B7/s** to the epoxide precursor has an activation barrier of 33.76 kcal/mol and reaction energy of +3.62 kcal/mol. Also, the formation of the epoxide precursor through direct [2 + 1] addition of the $\text{C}=\text{C}$ bond of ethylene across one oxygen atom of TcO_3Cl has an activation barrier of 28.96 kcal/mol and a reaction energy of +4.03 kcal/mol. The barrier along this route is only 3.11 kcal/mol higher than the barrier for the metallaoyxetane formation by [2 + 2]_{Tc-O} addition; these steps are therefore competitive with each other. The epoxide precursor can also be formed from the re-arrangement of the doublet organometallic **X/d** through transition state **TS-[X-E]/d**. This path has an activation barrier of

14.46 kcal/mol and reaction energy of -9.64 kcal/mol. This pathway is the lowest energy route to the formation of the epoxide precursor.

Even though the formation of the dioxylyate on the singlet and doublet PES is kinetically and thermodynamically favorable, the barrier for the formation of the dioxylyate on the doublet PES is twice that on the singlet PES and thus the formation of the dioxylyate would most likely occur on the singlet PES.

3.3. Reaction of $\text{TcO}_3(\text{NPH}_3)$ with ethylene

Fig. 3 shows the main stationary points involved in the reaction between $\text{TcO}_3(\text{NPH}_3)$ and ethylene and some of the optimized structures. A singlet $\text{TcO}_3(\text{NPH}_3)$ reactant is 47.79 kcal/mol more stable than the triplet reactant while the doublet $\text{TcO}_3(\text{NPH}_3)$ reactant is 55.69 kcal/mol more stable than the quartet reactant.

Singlet and doublet transition states have been located for the formation of the dioxylyate intermediate through the [3 + 2] addition of the $\text{C}=\text{C}$ bond of ethylene across the $\text{O}=\text{Tc}=\text{O}$ bonds of singlet and doublet $\text{TcO}_3(\text{NPH}_3)$. If the reaction proceeds from the singlet reactant through the singlet transition state to a singlet product, the activation barrier is 15.36 kcal/mol and the reaction energy is -20.22 kcal/mol. If on the other hand, it proceeds from a doublet reactant through the doublet transition state to a doublet

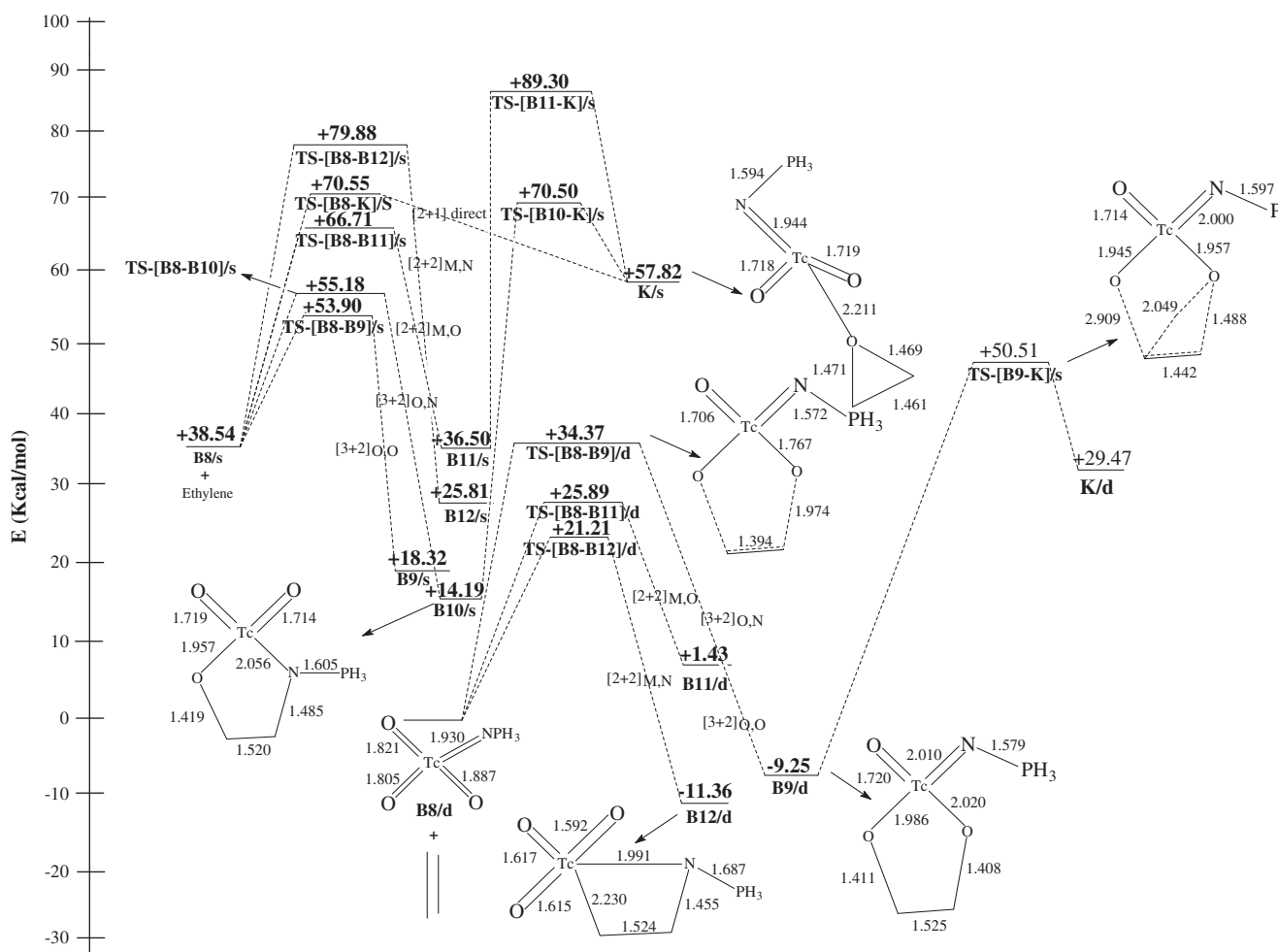


Fig. 3. Energetics of the reactions of $\text{TcO}_3(\text{NPH}_3)$ with ethylene (s = singlet, d = doublet). (Note that the singlet structures and the doublet structures are not isoelectronic and therefore their energies are not to be compared directly.)

product, the activation barrier is 34.37 kcal/mol and the reaction energy is -9.25 kcal/mol. A triplet dioxylate has been found to be 46.14 kcal/mol more stable than the singlet.

The [3 + 2] addition of the C=C bond of ethylene across the O=Tc=N bonds of singlet $\text{TcO}_3(\text{NPH}_3)$ through the singlet transition state **TS-[B8-B10]/s** to form the five-membered metallacycle **B10/s** has an activation barrier of 16.64 kcal/mol and a reaction energy of -24.35 kcal/mol. Thus the [3 + 2]_{N,O} addition route is only 1.28 kcal/mol higher in activation energy than the [3 + 2]_{O,O} addition route. The triplet five-membered species is 32.57 kcal/mol more stable than the singlet species while the quartet species is 42.51 kcal/mol more stable than the doublet species. The triplet and quartet structures have an O–P bond with O–P bond lengths of 1.88 and 1.790 Å respectively.

The formation of the singlet metallaoxetane through a singlet transition state by [2 + 2] addition of the C=C bond of ethylene across the Tc=O bond of singlet $\text{TcO}_3(\text{NPH}_3)$ has an activation barrier of 28.17 kcal/mol and reaction energy of -2.04 kcal/mol while the formation of the doublet metallaoxetane through the doublet transition state has an activation barrier of 25.89 kcal/mol and reaction energy of +1.43 kcal/mol. The triplet metallaoxetane has been found to be 11.28 kcal/mol more stable than the singlet one while the doublet metallaoxetane is 11.29 kcal/mol more stable than the quartet one.

A search of the surface for the reaction for the re-arrangement of the metallaoxetane to the dioxylate (i.e. **TS-[4-2]** in Scheme 1) did not yield any positive results.

The [2 + 2] addition of ethylene across the Tc=N bond of $\text{TcO}_3(\text{NPH}_3)$ on the singlet, doublet, and triplet surfaces results in products in which there is an O–P bond between a ring O atom and phosphine P atom. The formation of the singlet four membered metallacycle by [2 + 2] addition of the C=C bond of ethylene across the Tc=N bond of singlet $\text{TcO}_3(\text{NPH}_3)$ through the singlet transition state has an activation barrier of 41.34 kcal/mol and reaction energy of -12.73 kcal/mol. The formation of the doublet species through doublet transition state has an activation barrier of 21.21 kcal/mol and reaction energy of -11.36 kcal/mol. The triplet product is 7.73 kcal/mol less stable than the singlet species. No triplet transition state could be located.

A search on the reaction surface for the re-arrangement of the four-membered metallacycle to the five-membered metallacycle (i.e. **TS-[5-6]** in Scheme 1) yielded no positive results.

The re-arrangement of the singlet five-membered metallacycle **B10/s** to the epoxide precursor through transition state **TS-[B10-K]/s** has an activation barrier of 56.31 kcal/mol and reaction energy of +43.63 kcal/mol while the re-arrangement of the singlet five-membered metallacycle **B9/s** through transition state **TS-[B9-K]/s** to the epoxide precursor has an activation barrier of 70.04 kcal/mol and a reaction energy of +39.50 kcal/mol. The re-arrangement of the singlet four-membered metallaoxetane to the epoxide precursor through transition state **TS-[B11-K]/s** has an activation barrier of 52.80 and reaction energy of 21.32 kcal/mol. The singlet direct one-step [2 + 1] addition of the C=C bond across one oxygen atom of $\text{TcO}_3(\text{NPH}_3)$ to form the epoxide precursor has an activa-

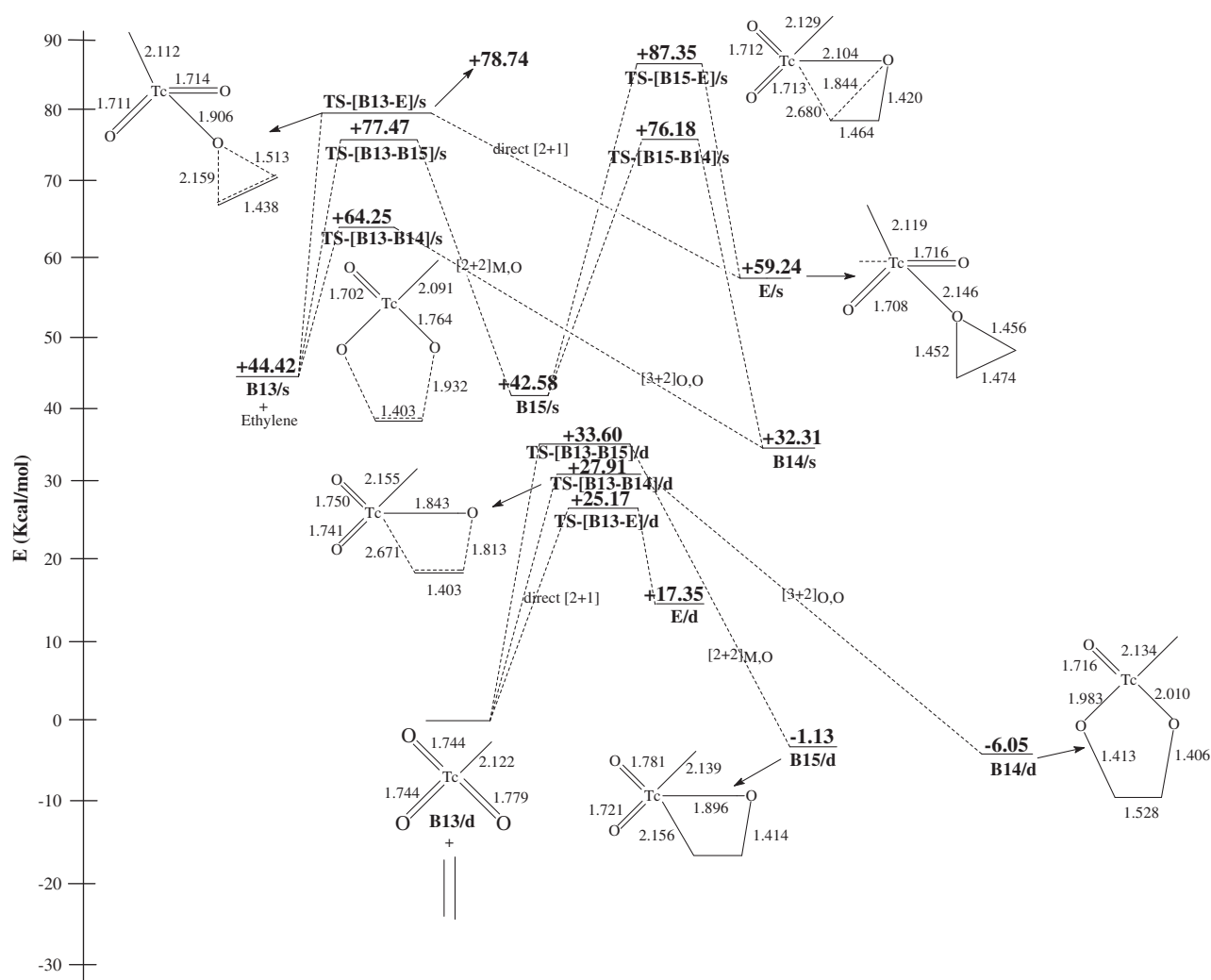


Fig. 4. Energetics of the reactions of $\text{TcO}_3(\text{CH}_3)$ with ethylene (s = singlet, d = doublet). (Note that the singlet structures and the doublet structures are not isoelectronic and therefore their energies are not to be compared directly.)

tion barrier of 32.01 kcal/mol and reaction energy of +19.28 kcal/mol. Therefore, the most plausible pathway for the formation of the epoxide precursor is by the direct [2 + 1] addition pathway.

From the energetics of the reaction displayed in Fig. 3, the addition of $\text{TcO}_3(\text{NPH}_3)$ to ethylene is likely to occur on the singlet PES and the [3 + 2] addition of ethylene across the $\text{O}=\text{Tc}=\text{O}$ bond of singlet $\text{TcO}_3(\text{NPH}_3)$ to form the dioxyate intermediate is kinetically and thermodynamically most favorable.

3.4. Reaction of $\text{TcO}_3(\text{CH}_3)$ with ethylene

The optimized geometries and relative energies of the main stationary points involved in the reaction between $\text{TcO}_3(\text{CH}_3)$ and ethylene are shown in Fig. 4. The $\text{TcO}_3(\text{CH}_3)$ has singlet, doublet, triplet and quartet ground state electronic structures. The singlet structure is 49.75 kcal/mol more stable than the triplet structure while doublet structure is 72.34 kcal/mol more stable than the quartet structure.

The activation barrier and reaction energy for the [3 + 2] addition of the $\text{C}=\text{C}$ bond of ethylene across the $\text{O}=\text{Tc}=\text{O}$ bond of singlet $\text{TcO}_3(\text{CH}_3)$ through a singlet transition state has been computed to be 19.83 and -12.11 kcal/mol respectively. Gisdakis and Rösch [25] calculated the barrier along this route to be 23.70 kcal/mol. The [3 + 2] addition of the $\text{C}=\text{C}$ bond of ethylene

across the $\text{O}=\text{Tc}=\text{O}$ bond of doublet $\text{TcO}_3(\text{CH}_3)$ through a doublet transition state to form the dioxyate has an activation barrier of 27.91 kcal/mol and reaction energy of -6.05 kcal/mol. The triplet dioxyate species is 57.41 kcal/mol more stable than the singlet species while the quartet dioxyate species is 9.18 kcal/mol more stable than the doublet. No triplet or quartet transition state linking the reactants to the products could be located on the reaction surfaces.

The formation of the singlet metallaoxetane through a transition state by [2 + 2] addition of the $\text{C}=\text{C}$ bond of ethylene across the $\text{Tc}=\text{O}$ bond of singlet $\text{TcO}_3(\text{CH}_3)$ has an activation barrier of 33.05 kcal/mol and reaction energy of -1.84 kcal/mol. The formation of the doublet metallaoxetane by [2 + 2] addition of the $\text{C}=\text{C}$ bond of ethylene across the $\text{Tc}=\text{O}$ bond of doublet $\text{TcO}_3(\text{CH}_3)$ through a doublet transition state has an activation barrier of 33.60 kcal/mol and reaction energy of -1.13 kcal/mol.

The re-arrangement of the singlet metallaoxetane to the singlet dioxyate through a singlet transition state has a barrier of 33.60 kcal/mol. No doublet, triplet or quartet transition state was located for re-arrangement of the metallaoxetane to dioxyate. Thus the activation barrier for the re-arrangement of the singlet metallaoxetane to the dioxyate is higher than the activation barrier for the direct [3 + 2] addition of $\text{C}=\text{C}$ π of ethylene across $\text{O}=\text{Tc}=\text{O}$ of singlet $\text{TcO}_3(\text{CH}_3)$. This rules out the two-step process

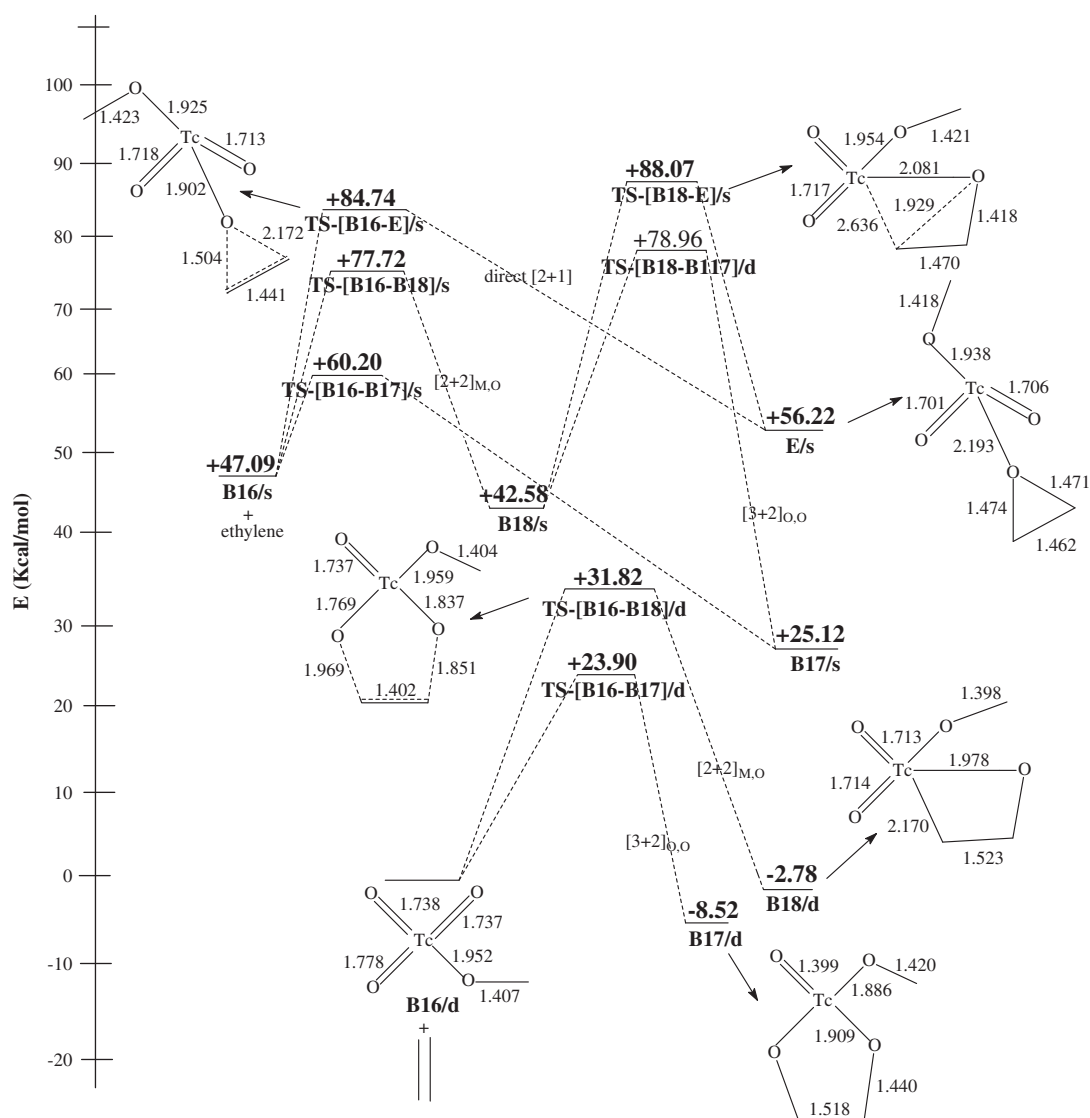


Fig. 5. Energetics of the reactions of $\text{TcO}_3(\text{OCH}_3)$ with ethylene ($s = \text{singlet}$, $d = \text{doublet}$). (Note that the singlet structures and the doublet structures are not isoelectronic and therefore their energies are not to be compared directly.)

for the formation of the dioxylate through the metallaoxetane. The dioxylate would be formed from the direct $[3 + 2]$ addition of ethylene across the two oxygen atoms of $\text{TcO}_3(\text{CH}_3)$.

The reaction of $\text{TcO}_3(\text{CH}_3)$ with ethylene was explored for the formation of an epoxide precursor. The re-arrangement of the singlet four-membered metallaoxetane to the epoxide precursor through the singlet transition state **TS [B15-E]/s** has an activation barrier of 44.77 kcal/mol and reaction energy of +16.66 kcal/mol. No transition state could be located for the re-arrangement of the five-membered metallacycle intermediate to the epoxide precursor. The formation of the singlet epoxide precursor from direct attack of the $\text{C}=\text{C}$ bond on the oxygen atom of $\text{TcO}_3(\text{CH}_3)$ in a $[2 + 1]$ addition mode has been found to have an activation barrier of 34.32 kcal/mol and reaction energy of +14.82 kcal/mol. The barrier for this route is only 1.27 kcal/mol higher than the barrier for the metallaoxetane formation; this might lead to a competition between the two reactions. On the doublet surface, the activation barrier and reaction energy are 25.17 and +17.35 kcal/mol respectively. The difference in activation energy between this route and the dioxylate formation route is only 2.74 kcal/mol (Fig. 4); thus these steps might compete. The triplet epoxide precursor is 45.59 kcal/mol more stable than the singlet species while the quar-

ter structure is 15.95 kcal/mol more stable than the doublet structure. Therefore, the most plausible pathway for the formation of the epoxide precursor is by direct $[2 + 1]$ addition on the doublet surface.

3.5. Reaction of $\text{TcO}_3(\text{OCH}_3)$ with ethylene

The optimized geometries of the reactants, transition states, intermediates and products, involved in the reaction between $\text{TcO}_3(\text{OCH}_3)$ and ethylene and the energetics of the reaction are shown in Fig. 5. Singlet, doublet, triplet and quartet species have been optimized for the reactant $\text{TcO}_3(\text{OCH}_3)$. The singlet reactant is 51.82 kcal/mol more stable than the triplet while the doublet reactant is 46.43 kcal/mol more stable than the quartet reactant.

The $[3 + 2]$ addition of the $\text{C}=\text{C}$ bond of ethylene across the $\text{O}=\text{Tc}=\text{O}$ bond of singlet $\text{TcO}_3(\text{OCH}_3)$ through a singlet transition state to form the singlet dioxylate has an activation barrier of 13.11 kcal/mol and reaction energy of -21.97 kcal/mol. The $[3 + 2]$ addition of the $\text{C}=\text{C}$ bond of ethylene across the $\text{O}=\text{Tc}=\text{O}$ bond of doublet $\text{TcO}_3(\text{OCH}_3)$ through a doublet transition state to form the doublet dioxylate has an activation barrier of 23.90 kcal/mol and reaction energy of -8.52 kcal/mol. The triplet

dioxylate intermediate is 93.68 kcal/mol more stable than the singlet dioxylate while the quartet dioxylate is 32.97 kcal/mol more stable than the doublet dioxylate.

The formation of the singlet metallaoxetane by [2 + 2] addition of the C=C bond of ethylene across the Tc=O bond of singlet $\text{TcO}_3(\text{OCH}_3)$ through a singlet transition state has an activation barrier of 30.63 kcal/mol and reaction energy of -4.51 kcal/mol while the formation of the doublet metallaoxetane through the transition state by [2 + 2] addition of the C=C bond of ethylene across the Tc=O bond of doublet $\text{TcO}_3(\text{OCH}_3)$ has an activation barrier of 31.82 kcal/mol and reaction energy of 2.78 kcal/mol. The re-arrangement of the metallaoxetane to the dioxylate was explored for the reaction of $\text{TcO}_3(\text{OCH}_3)$ with ethylene but no transition states were located for this re-arrangement.

An epoxide precursor was optimized from the reaction of $\text{TcO}_3(\text{OCH}_3)$ with ethylene. The re-arrangement of the singlet four-membered metallaoxetane to the epoxide precursor through singlet transition state **TS [B18-E]/s** has an activation barrier of 45.49 kcal/mol and reaction energy of $+13.64$ kcal/mol. The formation of the singlet epoxide precursor from direct attack of the C=C bond on the oxygen atom of $\text{TcO}_3(\text{CH}_3)$ in a [2 + 1] mode has been computed to have a barrier of 37.65 kcal/mol and reaction energy of $+9.13$ kcal/mol. No transition state could be located for the conversion of the five-membered metallacycle to the epoxide precursor. Therefore, the most plausible pathway for the formation of the epoxide, if it is to form at all, is by direct [2 + 1] addition on the singlet surface.

3.6. Reaction of TcO_3Cp with ethylene

Fig. 6 shows the relative energies of the main stationary points involved in the reaction between TcO_3Cp and ethylene as well as

some of the optimized structures. The singlet reactant has Tc=O bond lengths of 1.72 Å. The cyclopentadienyl ligand (Cp) is bonded to the metal center in a η^5 fashion i.e. Tc–C (Cp) = 2.486, 2.492, 2.492, 2.483 and 2.503 Å. For MnO_3Cp , Gisdakis and Rösch [25] found, by means of DFT B3LYP/LanL2DZ calculations, the Cp ligand to be bound to the metal center in η^1 fashion. No doublet, triplet and quartet reactants could be located.

The [3 + 2] addition of C=C bond of ethylene across the O=Tc=O bonds of singlet TcO_3Cp through a singlet transition state to form a singlet metalladioxolane intermediate has an activation barrier of 2.66 kcal/mol and reaction energy of -46.50 kcal/mol, which is in agreement with the activation barrier and reaction energy reported by Gisdakis and Rösch [25] at the B3LYP/LanL2DZ, 6-311G(d,p) level of theory. The calculated transition state is highly synchronous with respect to the newly forming C–O bonds. The Cp ligand in the singlet [3 + 2] transition state structure shows η^5 – bonding to the metal center (i.e. Tc–C (Cp) = 2.358, 2.455, 2.463, 2.628, 2.635 Å). The Cp ligand in the singlet TcO_3Cp -dioxylate **B20/s** also shows a η^5 – bonding fashion to the Tc center (Tc–C (Cp) = 2.348, 2.359, 2.422, 2.502, 2.545 Å). The singlet dioxylate has been found to be 11.80 kcal/mol more stable than the triplet dioxylate. The Cp ligand in the triplet TcO_3Cp -dioxylate also shows η^5 – bonding fashion to the Tc center (Tc–C (Cp) = 2.318, 2.412, 2.466, 2.536 and 2.581 Å). The doublet dioxylate is 11.59 kcal/mol more stable than the quartet dioxylate. In the doublet dioxylate, the Cp ligand shows η^5 – bonding fashion to the Tc center (Tc–C (Cp) = 2.323, 2.571 and 2.617, 2.437, 2.298 Å). The Cp ligand in the quartet TcO_3Cp -dioxylate shows η^5 – bonding fashion to the Tc center (Tc–C (Cp) = 2.424, 2.733, 2.998, 2.865, 2.518 Å).

On the singlet PES, the formation of the manganooxetane through the transition state **TS-[B19-B21]/s** by [2 + 2] addition of

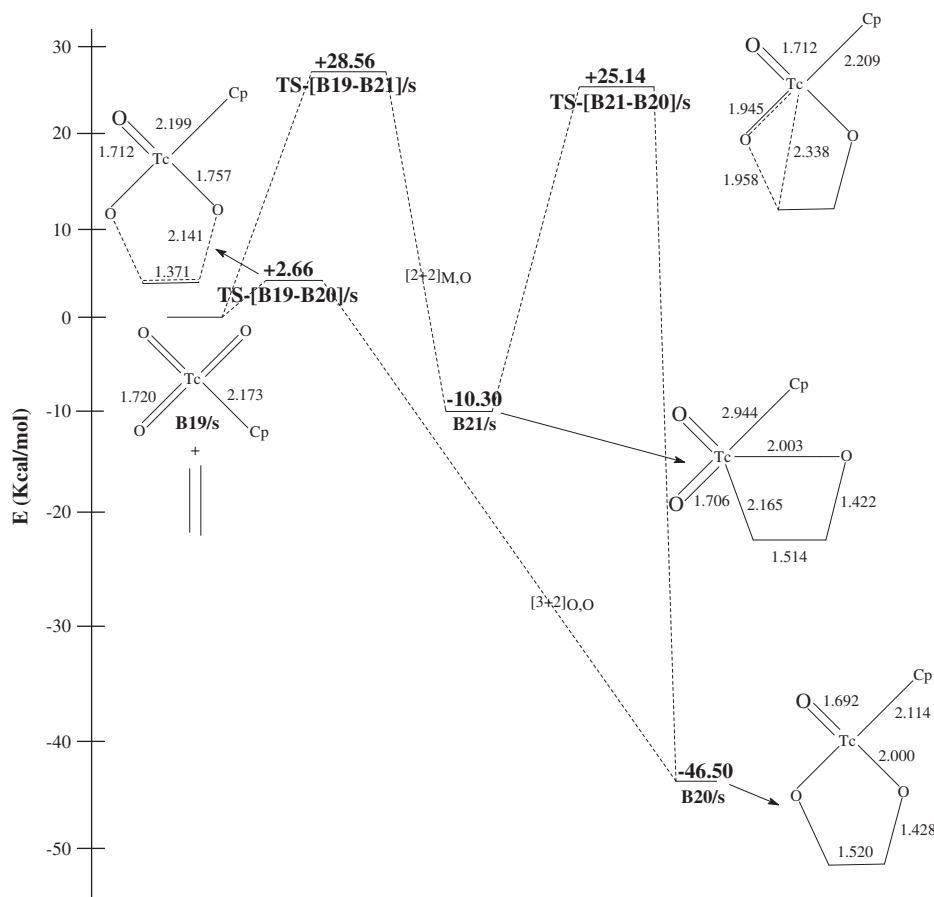


Fig. 6. Energetics of the reactions of $\text{TcO}_3(\text{OCH}_3)$ with ethylene. Relative energies in kcal/mol.

C=C bond of ethylene across the Tc=O bond of the TcO₃Cp complex has an activation barrier of 28.56 kcal/mol and reaction energy of –10.30 kcal/mol. The Cp ligand in the singlet [2 + 2] transition state structure shows η^3 – bonding to the metal center (i.e. Tc–C (Cp) = 2.191, 2.843, 2.883, 3.556 and 3.577 Å). The Cp ligand in the singlet TcO₃Cp-oxetane **B21/s** shows a η^3 – bonding mode to the Tc center, (Tc–C (Cp) = 2.907, 2.190, 2.999, 3.798, 3.750 Å), contrary to the η^5 – bonding mode in the singlet reactant **B19/s**. A triplet species with a metallaioxetane-like structure but with an elongated metal–oxygen bond has been optimized and found to be 26.62 kcal/mol less stable than the singlet. The Cp ligand in the triplet TcO₃Cp – oxetane shows a η^5 – bonding mode to the Tc center, (Tc–C (Cp) = 2.327, 2.520, 2.727, 2.696 and 2.482 Å).

The re-arrangement of the singlet metallaioxetane to the singlet dioxylate through singlet transition state **TS-[B21-B20]/s** has an activation barrier of 12.89 kcal/mol. No doublet, triplet and quartet transition states were located for re-arrangement of the metallaioxetane to the dioxylate. Thus the activation barrier for the re-arrangement of the singlet metallaioxetane to the dioxylate is higher than the activation barrier for the initial [3 + 2] addition of C=C π of ethylene across O=Tc=O of singlet and doublet TcO₃Cp. Thus, the dioxylate intermediate would be formed from the direct addition of ethylene across the two oxygen atoms of singlet TcO₃Cp rather than the re-arrangement of the metallaioxetane.

The potential energy surface of the reaction of TcO₃Cp with ethylene was further explored in an attempt to locate an epoxide precursor (O₂(Cp)–Tc–OC₂H₄) (structure **3** in Scheme 1), but no such minimum was found on these reaction surfaces.

4. Conclusion

The following conclusions are drawn from the results presented.

- In the reaction of ethylene with TcO₄[–] and TcO₃Cp, the direct [3 + 2] addition of the C=C bond of ethylene across the O=Tc=O bonds to form the dioxylate is kinetically and thermodynamically favored over the two-step reaction via the [2 + 2] addition across the Tc=O bond to form the metallaioxetane intermediate and subsequent re-arrangement to the dioxylate. The reaction of TcO₄[–] and TcO₃Cp with ethylene does not result in the formation of an epoxide precursor, which is in agreement with the works of Burrell et al. [22], Herrmann et al. [21], Klahn-oliva and Sutton [23] and Kühn et al. [24].
- In the oxidation of ethylene by TcO₃Cl on the singlet and doublet PES hyper surfaces, the direct [3 + 2] addition of the C=C bond of ethylene across the O=Tc=O bonds of TcO₃Cl to form the dioxylate intermediate is kinetically and thermodynamically favored over the formation of the metallaioxetane intermediate and subsequent re-arrangement to the dioxylate. The most plausible pathway that leads to the epoxide precursor is by the initial [3 + 2] addition of ethylene across the oxygen and chlorine atoms of TcO₃Cl followed by re-arrangement on the singlet PES.
- In the reaction between TcO₃(NPH₃) and ethylene, the direct [3 + 2] addition of the C=C bond of ethylene across the O=Tc=N and O=Tc=O bond of singlet TcO₃(NPH₃) to form the five-membered metallacycle are competitive kinetically and thermodynamically. On the doublet PES, the [2 + 2] addition of ethylene across the Tc=N bond of doublet TcO₃(NPH₃) to form the four-membered metallacycle is kinetically and thermodynamically favored over the formation of the five membered metallacycle. The most plausible pathway to the formation of the epoxide precursor is by the initial [3 + 2] addition across the oxygen and nitrogen atoms of singlet TcO₃(NPH₃) followed by re-arrangement on the singlet surface.
- In the oxidation of ethylene by TcO₃(CH₃), the direct [3 + 2] addition of the C=C bond of ethylene across the O=Tc=O bond of TcO₃(CH₃) to form the dioxylate intermediate on the singlet PES is kinetically and thermodynamically favored over the stepwise [2 + 2] addition to form the dioxylate. On the singlet and doublet PES, the most plausible pathway to the formation of the epoxide precursor is by direct attack of ethylene on one of the oxo ligand of singlet and doublet TcO₃(CH₃) in a [2 + 1] mode.
- In the oxidation of ethylene by TcO₃(OCH₃), the direct [3 + 2] addition of ethylene across the two oxygen atoms of TcO₃(OCH₃) on the singlet and doublet PES is kinetically and thermodynamically favored over the two-step process via the [2 + 2] addition of the C=C bond of ethylene across the Tc=O bonds of doublet TcO₃(OCH₃) to form the metallaioxetane intermediate and subsequent re-arrangement to the dioxylate. The most plausible pathway to the formation of the epoxide precursor is by direct attack of the ethylene on one of the oxo ligand of singlet TcO₃(OCH₃).
- There does not appear to be a spin-crossover in any of the pathways studied.

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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.comptc.2013.01.006>.

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