

Ethylene addition to $\text{OsO}_3(\text{CH}_2)$ – A theoretical study

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Abstract

Quantum chemical calculations at the B3LYP/TZVP level of theory have been carried out for the initial steps of the addition reaction of ethylene to $\text{OsO}_3(\text{CH}_2)$. The calculations predict that there are two reaction channels with low activation barriers. The kinetically and thermodynamically most favored reaction is the $[3+2]_{\text{O,C}}$ addition which has a barrier of only $2.3 \text{ kcal mol}^{-1}$. The $[3+2]_{\text{O,O}}$ addition has a slightly higher barrier of $6.5 \text{ kcal mol}^{-1}$. Four other reactions of $\text{OsO}_3(\text{CH}_2)$ with C_2H_4 have significantly larger activation barriers. The addition of ethylene to one oxo group with concomitant migration of one hydrogen atom from ethylene to the methylene ligand yields thermodynamically stable products but the activation energies for the reactions are 16.7 and $20.9 \text{ kcal mol}^{-1}$. Even higher barriers are calculated for the $[2+2]$ addition to the $\text{Os}=\text{O}$ bond ($32.6 \text{ kcal mol}^{-1}$) and for the addition to the oxygen atom yielding an oxiran complex ($41.2 \text{ kcal mol}^{-1}$). The activation barriers for the rearrangement to the bisoxosmaoxirane isomer ($36.3 \text{ kcal mol}^{-1}$) and for the addition reactions of the latter with C_2H_4 are also quite high. The most favorable reactions of the cyclic isomer are the slightly exothermic $[2+2]$ addition across the $\text{Os}=\text{O}$ bond which has an activation barrier of $46.6 \text{ kcal mol}^{-1}$ and the $[3+2]_{\text{O,O}}$ addition which is an endothermic process with an activation barrier of $44.3 \text{ kcal mol}^{-1}$.

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1. Introduction

The *cis*-dihydroxylation of olefins by OsO_4 is a reaction of practical importance in synthetic organometallic chemistry [1]. The development of catalytic protocols and the use of chiral bases for unsymmetric olefins provides efficient access to the chiral world such that the osmium-catalyzed asymmetric dihydroxylation has great synthetic potential [2]. The question about the reaction mechanism of the addition of OsO_4 to olefins was the topic of a long standing controversy which was finally resolved with the help of quantum chemical investigations [3]. Other theoretical studies of the addition of a metal–ligand double bond to

an olefin investigated the competition between a concerted $[3+2]$ addition and a two-step mechanism with initial $[2+2]$ addition for systems which are related to the addition of OsO_4 to olefins [4,5]. In a recent theoretical work we investigated the chemo- and regioselectivity in the addition of $\text{OsO}_2(\text{CH}_2)_2$ to ethylene [5]. The calculations revealed that the experimentally unknown bisalkylidene $\text{OsO}_2(\text{CH}_2)_2$ rearranges to the osmaoxirane $(\text{CH}_2)\text{Os}(\text{=O})(\text{cyc-OCH}_2)$ prior to the $[2+2]$ addition. Another energetically low-lying rearrangement, which opens new reaction pathways, was the formation of the bisoxosmacyclopropane species $\text{O}_2\text{Os}(\text{C}_2\text{H}_4)$. The energetically most favorable reactions were the $[3+2]$ additions of $\text{OsO}_2(\text{CH}_2)_2$ via C,C-, C,O-, and O,O-addition to ethylene. Our earlier results [5] showed that the rearrangement of $\text{OsO}_2(\text{CH}_2)_2$ through C–C and C–O coupling reactions make the mechanism of the addition reaction to ethylene quite complicated

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and unveiled an overall reaction profile for the addition of $\text{OsO}_2(\text{CH}_2)_2$ to olefins that is much more complicated than that of OsO_4 [5].

With only one methylene group and three oxo functionalities the key species of our present study, the osmiumtrioxomethylene **1**, represents a somewhat simpler system with respect to its reactivity against ethylene. We calculated the transition states and intermediates for the initial steps of the addition reaction of osmiumtrioxomethylene to ethylene. In order to support future experimental work we present the theoretically predicted reaction profile of the rearrangements of $\text{OsO}_3(\text{CH}_2)$ and the [2+2] and [3+2] addition to C_2H_4 yielding various reaction products.

2. Computational details

Density functional calculations have been performed employing the B3LYP hybrid functional [6] as implemented [7] in the Gaussian03 program [8]. The TZVP all-electron basis was used for C, O, and H atoms [9]. For Os, the Stuttgart/Köln relativistic effective core potential replacing 60 core electrons was used in combination with a (311111/22111/411) valence basis set [10]. Analytically evaluated Hessians were used to characterize the nature of stationary points and to obtain zero-point vibrational energy contributions (ZPE). All connectivities between minima and transition structures implied in the figures below were carefully verified by intrinsic reaction coordinate following (IRC) [11] calculations at this level of theory. The relative energies discussed below include unscaled ZPE contributions.

3. Results and discussion

To assess the potential occurrence of the experimentally unknown osmiumtrioxomethylene **1** as reactive intermediate in addition reactions with ethylene we first studied a number of conceivable isomerization processes illustrated in Fig. 1.

The calculations predict that the energetically most favorable pathway for isomerization occurs through coupling of the oxygen atom with the methylene group, which leads to formation of the osmaoxirane isomer **1a**. This species in fact is energetically significantly more stable than **1** (by $33.3 \text{ kcal mol}^{-1}$), but the isomerization is connected with a substantial barrier of $36.3 \text{ kcal mol}^{-1}$ (**TS1** → **1a**). Alternative O—O coupling in **1** leads to formation of the peroxy species **1b**, which is $41.3 \text{ kcal mol}^{-1}$ less stable than **1**. The corresponding energy barrier via **TS1** → **1b** is $72.6 \text{ kcal mol}^{-1}$. Subsequent formation of a C—O bond via **TS1b** → **1e** yields another energetically high lying isomer **1e**, which is also accessible from **1a** via O—O bond formation (**TS1a** → **1e**). Either of these pathways, however, is connected with prohibitively large barriers such that neither **1b** nor **1e** are likely to play any role in the course of the reaction (see Table 1).

Two further isomerization pathways leading to **1c** and **1d** might occur subsequent to the formation of **1a** with comparatively low barriers (Fig. 1), but both products are energetically less favorable than **1a**. We conclude that **1** is thermodynamically less stable than the osmaoxirane **1a**. However, the large energy barrier associated with the isomerization ($36.3 \text{ kcal mol}^{-1}$) implies that this process is

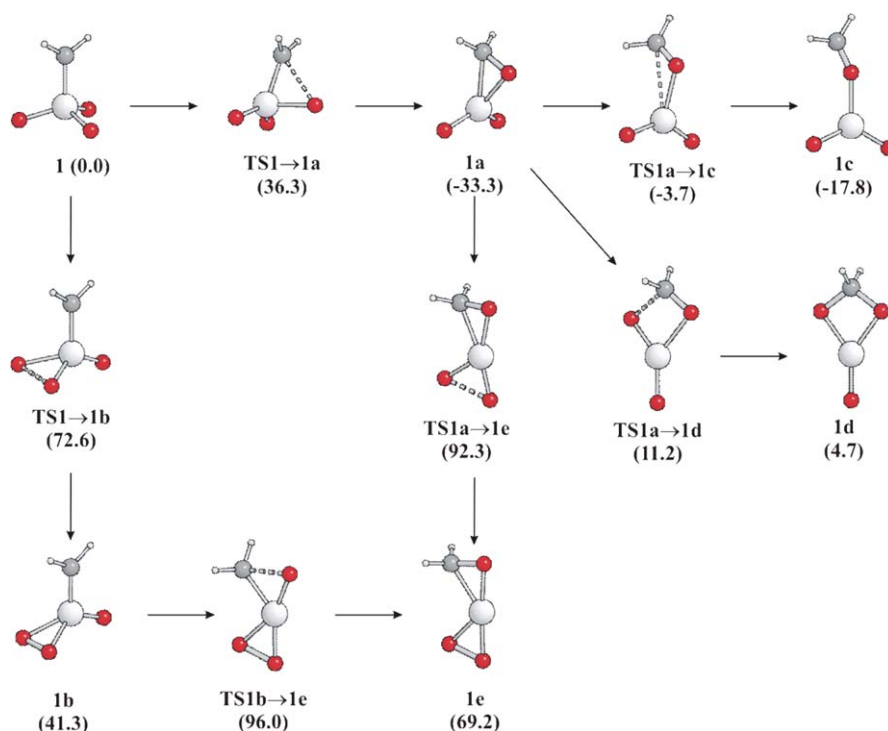


Fig. 1. Theoretically predicted isomerization pathways of **1**. Energies in kcal mol^{-1} .

Table 1
Calculated energies at B3LYP/TZVP

Structure	E_{tot}	ZPE	E_0^{rel}
C ₂ H ₄	-78.62155	0.05095	
1	-355.72813	0.03296	0.0
TS1 → 1a	-355.66999	0.03259	36.3
1a	-355.78483	0.03658	-33.3
TS1 → 1b	-355.61109	0.03167	72.6
1b	-355.66242	0.03300	41.3
TS1a → 1c	-355.73534	0.03422	-3.7
1c	-355.75900	0.03552	-17.8
TS1a-1d	-355.71281	0.03548	11.2
1d	-355.72484	0.03723	4.7
TS1a → 1e	-355.58221	0.03412	92.3
TS1b → 1e	-355.57462	0.03251	96.0
1e	-355.62054	0.03558	69.2
TS1 → 2	-434.34266	0.08725	6.5
2	-434.40596	0.09180	-30.4
TS1 → 3	-434.34894	0.08684	2.3
3	-434.45072	0.09426	-56.9
TS1 → 4	-434.30081	0.08694	32.6
4	-434.34995	0.09002	3.7
TS1a → 4	-434.30396	0.08695	30.6
TS1a → 5	-434.31568	0.08812	24.0
5	-434.37807	0.09170	-12.9
TS1a → 6	-434.33839	0.09013	11.0
6	-434.37193	0.09394	-7.7
TS1a → 7	-434.33367	0.08904	13.3
7	-434.41474	0.09252	-35.4
TS1b → 8	-434.26168	0.08574	56.4
8	-434.34856	0.08984	4.4
TS1c → 9	-434.30892	0.08680	27.4
9	-434.38036	0.09120	-14.7
10	-434.43199	0.09282	-46.1
TS10 → 11	-434.36470	0.09149	-4.7
11	-434.40547	0.09506	-28.0
12	-434.41888	0.09318	-37.6
TS12 → 13	-434.36379	0.09243	-3.5
13	-434.37072	0.09328	-7.3
TS1 → 14	-434.28669	0.08653	41.2
14	-434.31933	0.09001	22.9
TS1a → 15	-434.31016	0.08921	28.1
15	-434.32732	0.09237	19.3
TS1 → 16	-434.31540	0.08292	20.9
16	-434.42146	0.08917	-41.7
TS1 → 17	-434.32254	0.08342	16.7
17	-434.37310	0.08964	-11.1

Total energies (E_{tot}) and zero point vibrational energies (ZPE) are given in Hartree, relative energies in kcal mol⁻¹; E_0^{rel} include ZPE contributions.

kinetically hindered and **1** thus should in principle be identifiable as a reaction intermediate. Of course, this prediction is valid only for gas phase conditions as it is hard to estimate the influence of the oxidative environment present in homogeneous phase under the reaction conditions. It is quite clear, however, that both isomers must be considered as reactive intermediates for the addition of ethylene in the present study.

As the next step we investigated the addition reactions of ethylene. We identified three different pathways for the addition of C₂H₄ to **1** (Fig. 2). The [3+2] addition of ethylene to the O=Os=O group occurs via **TS1** → **2** with a rather low barrier of 6.5 kcal mol⁻¹ and results in the strongly exothermic formation of the methyleneoxosma-

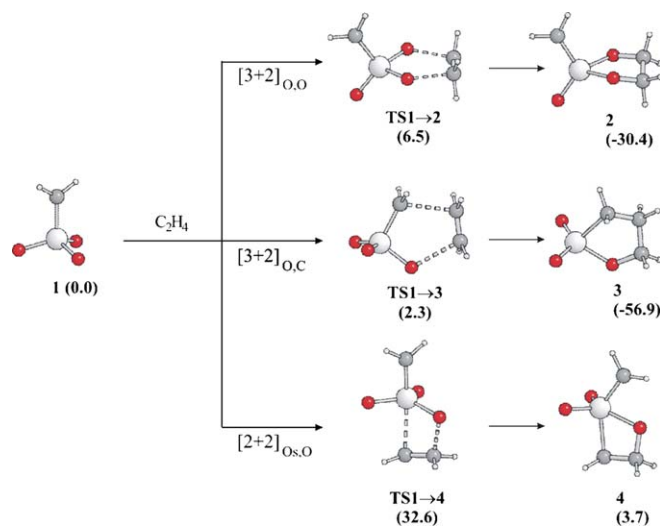


Fig. 2. Cycloaddition pathways for **1** + C₂H₄. Energies in kcal mol⁻¹.

2,5-dioxolane **2**, which is more stable than the separated reactants **1** + C₂H₄ by 30.4 kcal mol⁻¹. In line with the results of our recent study [5] we find the related [3+2] addition of ethylene to the O=Os=CH₂ group to form the dioxosma-2-oxolane **3** even more favored, both kinetically and thermodynamically. Compound **3** represents the most stable species among all minima investigated here. The corresponding barrier via **TS1** → **3** is only 2.3 kcal mol⁻¹ and the thermodynamic driving force of this process (-56.9 kcal mol⁻¹) is substantial. The [2+2] addition of ethylene across the Os=O bond, in turn, cannot compete with the former two processes. It occurs via a rather high barrier (**TS1** → **4**, 32.6 kcal mol⁻¹) and results in the endothermic formation of the methylenedioxosma-2-oxetane (**4**) (+3.7 kcal mol⁻¹ relative to **1** + C₂H₄). A corresponding transition state for the [2+2] addition across the Os=C bond was not found, all attempts to optimize such a structure lead to **TS1a** → **5** instead (see below).

Next we studied the addition pathways of ethylene to the osmaoxirane isomer **1a**. Among the four alternative routes identified, the [3+2] addition via **TS1a** → **6** constitutes the *kinetically* most favorable process although the activation barrier with respect to **1a** (44.3 kcal mol⁻¹) is quite high. Furthermore, the 2,5-dioxolane product **6** is *thermodynamically* significantly disfavored over **1a** (Fig. 3) and this reaction is endothermic by 25.6 kcal mol⁻¹. The [2+2] addition of ethylene across the Os=O bond via **TS1a** → **7** occurs with a slightly higher energy barrier (46.6 kcal mol⁻¹), but the formation of the very stable 2-oxolane species **7** renders this step slightly exothermic by -2.1 kcal mol⁻¹. We also identified two formal [2+2] additions of ethylene to the Os=O and Os=C bonds of **1a** leading to the products **4** and **5**, respectively. Both paths involve energetically demanding concerted transition states (>50 kcal mol⁻¹, **TS1a** → **4** and **TS1a** → **5**), in which formation of the new bonds is accompanied by a C–O bond cleavage within the osmaoxirane moiety.

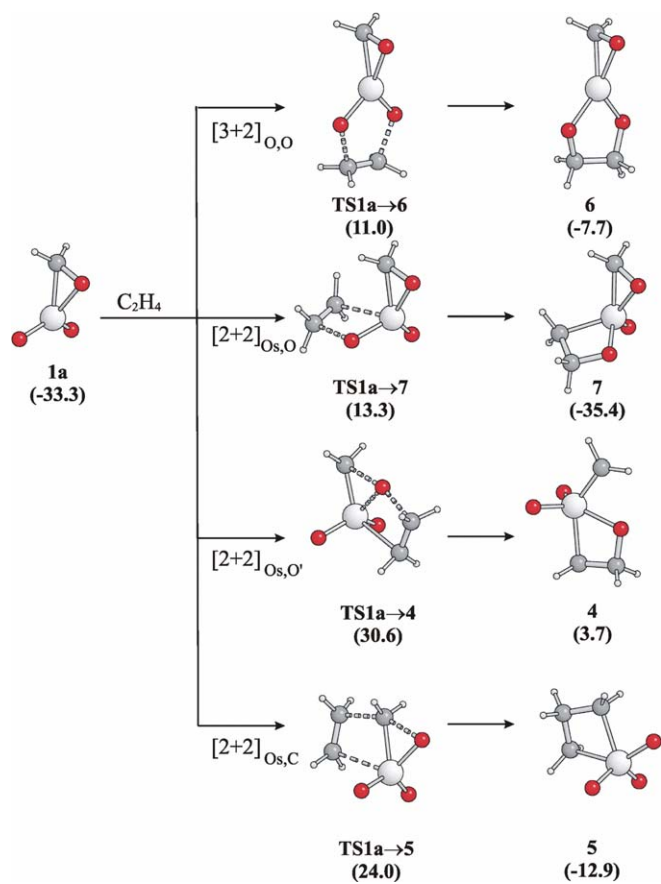


Fig. 3. Addition pathways for **1a** + C₂H₄. Energies in kcal mol⁻¹.

We also studied reaction pathways starting from other isomers of **1** (Figs. 4 and 5). The [2+2] addition of ethylene to the peroxo species **1b** also occurs via a concerted transition state **TS1b** → **8** and results in the formation of **8**, which represents a slightly less stable isomer of **4** (Fig. 4). The lack of stability of the peroxo isomer **1b** also leads to a prohibitively high reaction barrier such that this path is unlikely to play any role in the reaction scenario. A [2+2] reaction between ethylene and the formaldehyde complex **1c** yields the corresponding osma-2-oxetane complex **9**. This slightly endothermic process is connected with a large barrier of 45.2 kcal mol⁻¹ via **TS1c** → **9** and is thus strongly disfavored kinetically. We also identified a [3+2] reaction pathway **TS1c** → **18**, which should be of no relevance for the overall reactivity, due to its high energy barrier (66.6 kcal mol⁻¹) and endothermicity.

Finally, we found two pathways for the ethylene addition to **1d** (Fig. 5). Both routes start with the barrierless coordination of ethylene to form two rather stable intermediates **10** and **12**, in which ethylene is coordinatively bound to the metal. Subsequent C—O and C—Os bond formation via **TS10** → **11** and **TS12** → **13** lead to thermodynamically strongly disfavored products **11** and **13**, respectively. With the corresponding reaction barriers of 41.4 and 34.1 kcal mol⁻¹ both processes are unlikely to contribute to the overall reactivity.

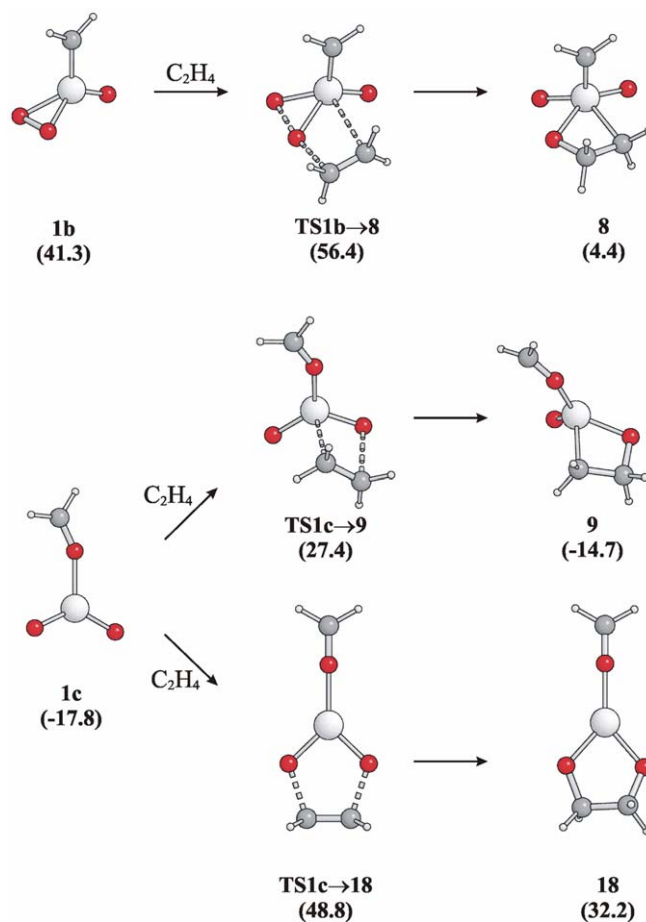


Fig. 4. Reaction pathways for (top) [2+2] ethylene addition to **1b** and (bottom) [2+2] and [3+2] ethylene addition to **1c**. Energies in kcal mol⁻¹.

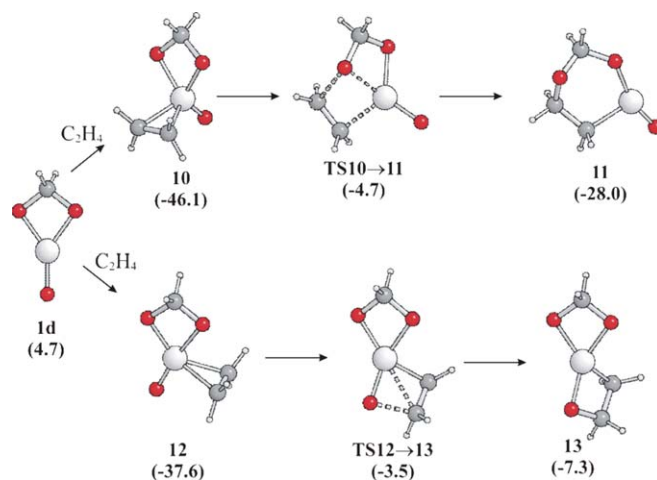


Fig. 5. Reaction pathways for the addition of ethylene to **1d**. Energies in kcal mol⁻¹.

In search of further alternative reaction pathways we discovered two rather unexpected routes, which correspond to a direct addition of ethylene to an oxo-ligand in **1** or **1a** leading to the epoxide complexes **14** and **15**, respectively (Fig. 6). However, both epoxidations cannot compete with

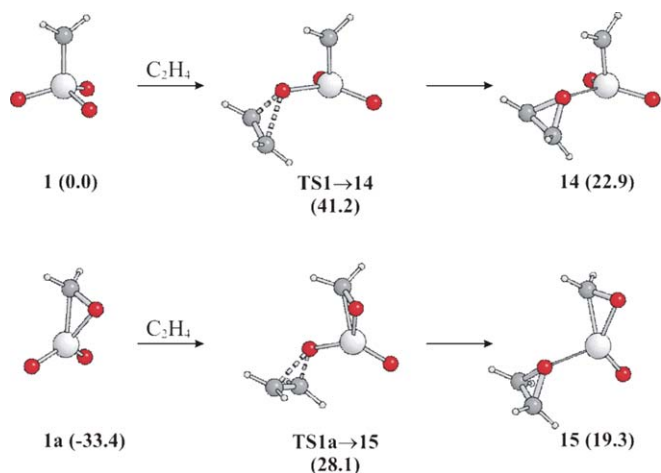


Fig. 6. Epoxidation pathways. Energies in kcal mol⁻¹.

the [3+2] or [2+2] routes identified above, neither kinetically nor thermodynamically.

Two other routes were found for the ethylene addition to **1**. One pathway occurs via **TS1** → **16**, which represents the transition state for a C–O bond formation with synchronous hydrogen transfer onto the carbene group (Fig. 7). With -41.7 kcal mol⁻¹ the thermodynamic driving force of this process is huge, but the barrier of 20.9 kcal mol⁻¹ renders this process kinetically disfavored compared to several other elementary steps identified above. Simultaneous formation of a C–O bond and hydrogen transfer in the opposite direction can occur via **TS1** → **17**, where the hydrogen atom is transferred onto the incoming ethylene group (Fig. 8). The barrier for this process is slightly lower (16.7 kcal mol⁻¹) than for the previous reaction but the product **17** is thermodynamically much less favored compared to **16**.

The calculated reaction pathways which are shown in Figs. 1–8 lead to an overall reaction profile for the initial

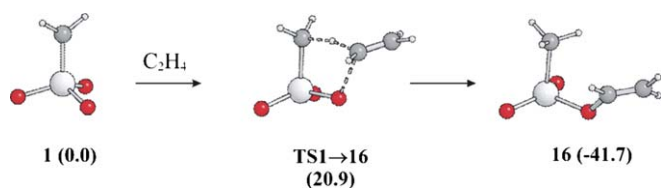


Fig. 7. Addition of ethylene to **1** with concomitant hydrogen migration from ethylene to the methylene. Energies in kcal mol⁻¹.

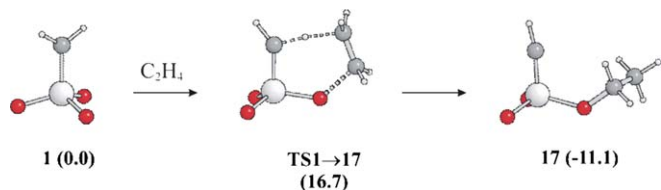


Fig. 8. Addition of ethylene to **1** with concomitant hydrogen migration from the methylene ligand to ethylene. Energies in kcal mol⁻¹.

steps of the addition of OsO₃(CH₂) to C₂H₄ shown in Fig. 9. The latter gives the energetically most favorable reactions of **1** and **1a** and further higher-lying reactions of the two molecules. The reaction pathways involving the isomers **1c–1e** are not shown in Fig. 9 because they cannot kinetically and thermodynamically compete with the energetically lowest lying processes.

The calculations predict two processes that are kinetically clearly favored over all other reactions. These are (a) the [3+2]_{O,C} addition of ethylene to **1** yielding the dioxosma-2-oxolane **3**, which is also the thermodynamically most stable reaction product of the initial addition reaction, and (b) the [3+2]_{O,O} addition **1** → **2** which has a slightly higher barrier (6.5 kcal mol⁻¹) than the [3+2]_{O,C} addition (2.3 kcal mol⁻¹). The latter process, however, is much less exothermic (-30.4 kcal mol⁻¹) than the former (-56.9 kcal mol⁻¹). The reaction **1** → **16** has a strong thermodynamic driving force (-41.7 kcal mol⁻¹) but the activation barrier (20.9 kcal mol⁻¹) is significantly higher than the two [3+2] addition reactions. The reaction **1** → **17** has a slightly lower barrier (16.7 kcal mol⁻¹) but the reaction is thermodynamically much less favored (-11.1 kcal mol⁻¹). The remaining endothermic reactions **1** → **4** and **1** → **14** have clearly higher barriers. The rather high barrier (36.3 kcal mol⁻¹) for the rearrangement **1** → **1a** indicates that the addition reactions of **1a** should not take place starting from isomer **1**. However, with **1a** as starting material the reaction with ethylene should take place only under severe conditions because the two kinetically favored pathways **1a** → **6** ([3+2]_{O,O} addition) and **1a** → **7** ([2+2] addition to Os=O) already have high barriers of 44.3 and 46.6 kcal mol⁻¹. Only the latter reaction is slightly exothermic while the other processes are endothermic. It is likely that, in the presence of oxidation means, the Os(VI) compound **1a** would rather be oxidized to a Os(VIII) compound which then undergoes further reactions. We will study such subsequent reaction steps in future work. Finally, we like to point out that the calculated reaction pathways shown in Fig. 9 clearly indicate the possibility to direct the reaction course by kinetic and thermodynamic control (compare **1** → **2** with **1** → **16** and **1a** → **6** with **1a** → **7**).

It is interesting to compare the results for the addition of OsO₃(CH₂) to C₂H₄ with the previous study about the addition reaction OsO₂(CH₂)₂ + C₂H₄ [5]. The calculations predict for both reactions that the [3+2]_{O,C} addition of ethylene to the respective Os(VIII) compound has the lowest activation barrier of all reactions. The activation energy for the [3+2]_{O,C} addition of OsO₂(CH₂)₂ is slightly higher (8.1 kcal mol⁻¹) than for OsO₃(CH₂) (2.3 kcal mol⁻¹). The kinetically less favored barrier 13.0 kcal mol⁻¹ [5] [3+2]_{C,C} addition reaction OsO₂(CH₂)₂ + C₂H₄ leads to the most stable product bisoxosmacyclopentane. A [3+2]_{C,C} addition is not possible for OsO₃(CH₂).

There is an interesting difference between the reactions of OsO₃(CH₂) and OsO₂(CH₂)₂ concerning the [2+2] addition of ethylene to the initial Os(VIII) compound.

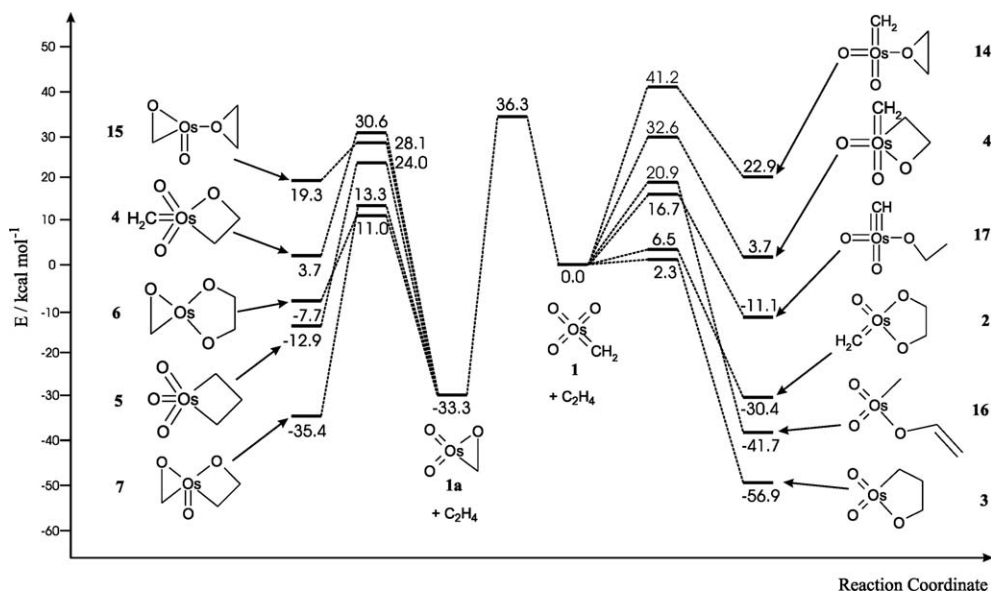


Fig. 9. Most important reaction steps for the addition of C_2H_4 to $OsO_3(CH_2)$.

No such reaction was found for $OsO_2(CH_2)_2$. The products of a formal [2+2] addition to the $Os=O$ and $Os=CH_2$ moieties are only formed via initial rearrangement of $OsO_2(CH_2)_2$ to the osmaoxirane isomer [5]. This is different to the reaction of $OsO_3(CH_2)$ where a [2+2] addition to the $Os=O$ double bond $1 \rightarrow 4$ (Fig. 2) could be identified through IRC calculations. For both $Os(VIII)$ molecules, $OsO_3(CH_2)$ and $OsO_2(CH_2)_2$, it holds that the rearrangements to the respective osmaoxirane isomer has rather high barriers. The activation energy for $OsO_2(CH_2)_2$ ($40.9 \text{ kcal mol}^{-1}$) is even higher than for $OsO_3(CH_2)$ ($36.3 \text{ kcal mol}^{-1}$).

4. Conclusions

The most important findings of this study can be summarized as follows. The quantum chemical calculations predict that the addition reaction of ethylene to $OsO_3(CH_2)$ has two reactions channels with low activation barriers. The kinetically and thermodynamically most favored reaction is the $[3+2]_{O,C}$ addition $1 \rightarrow 3$ which has a barrier of only $2.3 \text{ kcal mol}^{-1}$. The $[3+2]_{O,O}$ addition $1 \rightarrow 2$ has a slightly higher barrier of $6.5 \text{ kcal mol}^{-1}$. Four other reactions of 1 with C_2H_4 were identified with larger activation barriers. The addition of ethylene to one oxo group with concomitant migration of one hydrogen atom from ethylene to the methylene ligand $1 \rightarrow 16$ yields a thermodynamically low-lying product but the activation energy for the reaction is $20.9 \text{ kcal mol}^{-1}$. Simultaneous formation of a C–O bond and hydrogen transfer from the methylene ligand onto the incoming ethylene group via $TS1 \rightarrow 17$ has a slightly lower activation barrier of $16.7 \text{ kcal mol}^{-1}$ but the thermodynamic driving force is only $-11.1 \text{ kcal mol}^{-1}$. Rather high barriers are calculated for the [2+2] addition to the $Os=O$ bond $1 \rightarrow 4$ ($32.6 \text{ kcal mol}^{-1}$) and for the addition to the oxygen atom

yielding an oxiran complex $1 \rightarrow 14$ ($41.2 \text{ kcal mol}^{-1}$). The activation barriers for the rearrangement $1 \rightarrow 1a$ ($36.3 \text{ kcal mol}^{-1}$) and for the addition reactions $1a + C_2H_4$ are also quite high. The most favorable reactions of the bisoxosmaoxirane with ethylene are the slightly exothermic [2+2] addition across the $Os=O$ bond $1a \rightarrow 7$ which has an activation barrier of $46.6 \text{ kcal mol}^{-1}$ and the $[3+2]_{O,O}$ addition $1a \rightarrow 6$ which is an endothermic process with an activation barrier of $44.3 \text{ kcal mol}^{-1}$.

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