

Why Are Olefins Oxidized by RuO₄ under Cleavage of the Carbon–Carbon Bond whereas Oxidation by OsO₄ Yields *cis*-Diols?†

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Abstract: Quantum chemical calculations using gradient-corrected (B3LYP) density functional theory have been carried out to investigate the mechanism of the oxidative cleavage of alkenes by ruthenium tetraoxide. The initial reaction of the tetraoxide with the olefin occurs via a [3+2] cycloaddition as in the case of osmium tetraoxide. The results clearly show that the bond cleavage does not take place at the primary adduct, but much later in the reaction path. After the formation of the ruthenium(VI)dioxo-2,5-dioxolane, the reaction proceeds with the addition of a second olefin to yield ruthenium(IV)-bis(2,5-dioxolane), which in turn becomes oxidized first to rutheniumoxo(VI)-bis(2,5-dioxolane) **6(Ru)** and then to ruthenium(VIII)-dioxo-bis(2,5-dioxolane) **7(Ru)**. Only in complexes containing the metal center in the formal oxidation state +VIII are low activation barriers for C–C bond cleavage and exothermic formation of carbonyl compounds as products calculated. The lowest activation barrier, $\Delta H^\ddagger = 2.5$ kcal/mol, is calculated for the C–C bond breaking reaction of **7(Ru)** which is predicted as the pivotal intermediate of the oxidation reaction. The calculations of the oxidation reaction with OsO₄ show that those reactions where the oxidation state of the metal increases have larger activation barriers for M = Ru than for M = Os, while reactions which reduce the oxidation state have a lower activation barrier for ruthenium compounds. Also, reactions which increase the oxidation state of the metal are in the case of M = Os more exothermic than for M = Ru. In this work, all important points of the potential energy surface (PES) are reported, and the complete catalytic cycle for the oxidative cleavage of olefins by ruthenium tetraoxide is presented.

Introduction

The oxidation of olefins with osmium tetraoxide yielding *cis*-diols as oxidation products has been known since 1908 when it was first reported by Makowka.¹ The synthetic utility of the reaction was greatly extended by the systematic work of Sharpless who showed that, in the presence of chiral and sterically demanding amines such as chincinoa alkaloids, the reaction can proceed with high enantioselectivity.² Sharpless developed a catalytic variant of the OsO₄ addition to olefins which contributed further to the usefulness of the reaction. The mechanism of the asymmetric dihydroxylation was a topic of controversy for some time. It was initially thought that the reaction proceeds via a concerted [3+2] cycloaddition of osmium tetraoxide yielding a metalladioxo-2,5-dioxolane as the primary oxidation product.³ Sharpless suggested in 1977 that the reaction may take place via a [2+2] addition of the olefin across a Os=O double bond yielding a metallatrioxo-2-oxetane as the intermediate which then rearranges with little activation energy to the metalladioxo-2,5-dioxolane.⁴ Several quantum

chemical studies showed that the latter two-step reaction has very high activation barriers whereas the [3+2] addition proceeds with a low energy barrier.⁵ It is now generally accepted that the dihydroxylation of olefins with OsO₄ takes place via a concerted [3+2] cycloaddition.⁶

Ruthenium tetraoxide has long been known for being a much more vigorous oxidant than its osmium analogue, capable of readily cleaving carbon–carbon double bonds.⁷ The reaction can be carried out with catalytic amounts of RuO₄, which is neither explosive nor poisonous and therefore has advantages over the ozonolysis reaction and the carbon–carbon bond cleavage with chromium oxide. Although the reaction conditions can be tuned in such a way that *cis*-diols become the main product while the carbon–carbon bond cleavage is disfavored,⁸ the latter reaction which eventually yields carbonyl compounds as final products is usually observed. Because the reaction proceeds in most cases rapidly and under mild conditions, the

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(1) Makowka, O. *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 943.

(2) Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263.

(3) The first suggestion for a [3+2] mechanism was made by: Böeseken, J.; de Graaff, M. C. *Recl. Trav. Chim. Pays-Bas* **1922**, *41*, 199.

(4) Sharpless, K. B.; Teranishi, A. Y.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(5) (a) Pidun, U.; Boehme, C.; Frenking, G. *Angew. Chem.* **1996**, *108*, 3008; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2817. (b) Dapprich, S.; Ujaque, G.; Maseras, F.; Lledós, A.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1996**, *118*, 11660. (c) Torrent, M.; Deng, L.; Duran, M.; Sola, M.; Ziegler, T. *Organometallics* **1997**, *16*, 13. (d) Del Monte, A. J.; Haller, J.; Houk, K. N.; Sharpless, K. B.; Singleton, D. A.; Strassner, T.; Thomas, A. *J. Am. Chem. Soc.* **1997**, *119*, 9907.

(6) Deubel, D. V.; Frenking, G. *Acc. Chem. Res.* **2003**, *36*, 645.

(7) Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953**, *75*, 3838.

(8) Piccilli, V.; Smaldone, D. M. A.; Sica, D. *Tetrahedron* **1993**, *49*, 4211.

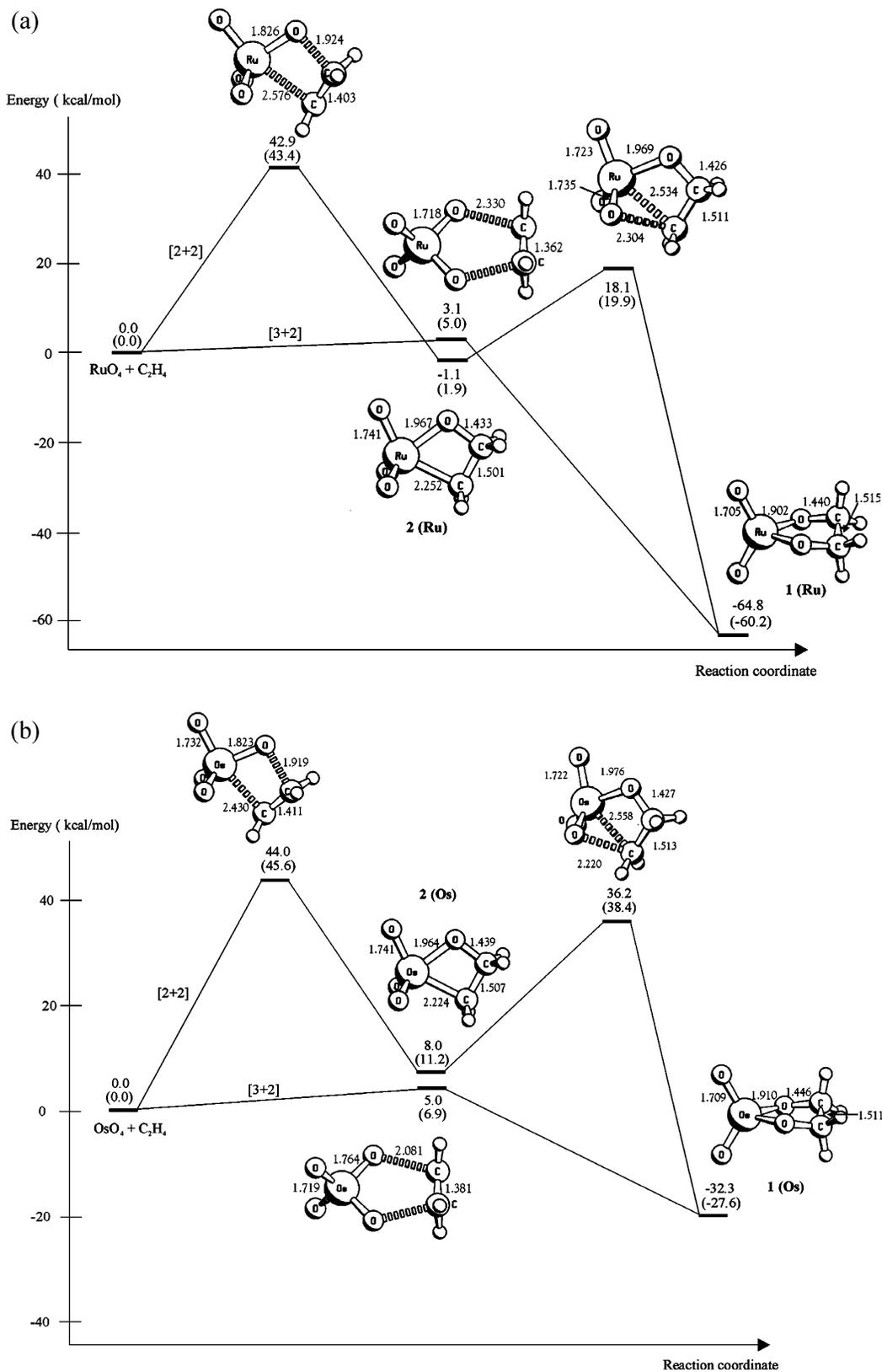


Figure 1. Calculated reaction profiles at B3LYP/II for the concerted [3+2] addition (reaction 1) of ethylene to the metal tetraoxide yielding **1(M)** and the two-step reaction with formation of **2(M)** as the intermediate. The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms. (a) Reaction of RuO₄. (b) Reaction of OsO₄.

activation barriers for the reaction steps yielding the final product must be low.

Unlike the oxidation of olefins with OsO₄, the mechanism of the reaction with RuO₄ has not been studied with quantum

chemical methods in detail until now. The only theoretical study which is known to us has been published by Norrby et al.⁹ These workers reported the structures and relative energies of the products of [3+2] and [2+2] addition of RuO₄ to ethylene. The

Scheme 1. Schematic Representation of the Formation of the Calculated Intermediates Which Have Been Considered as Precursors for the C–C Cleavage Reaction

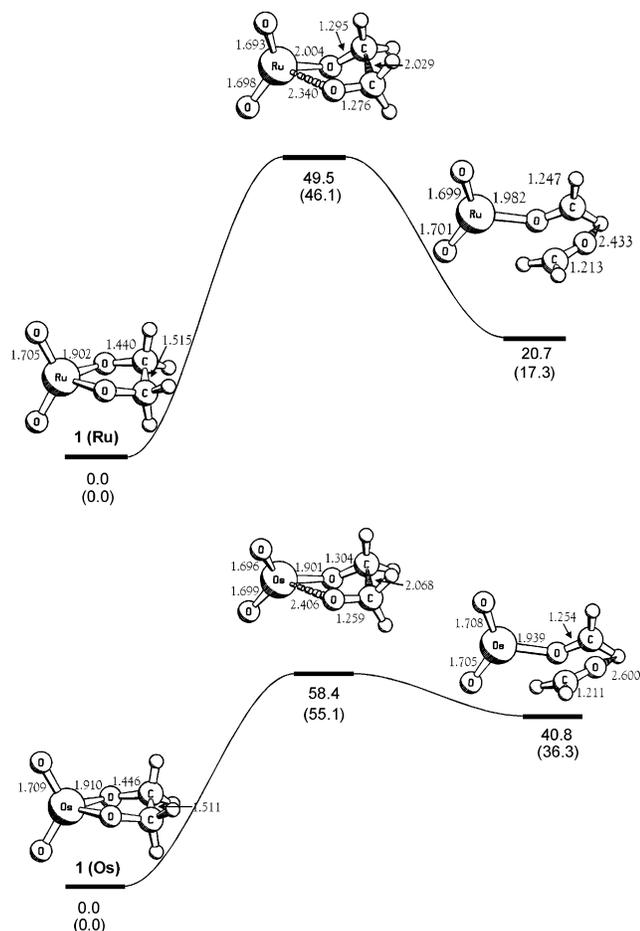
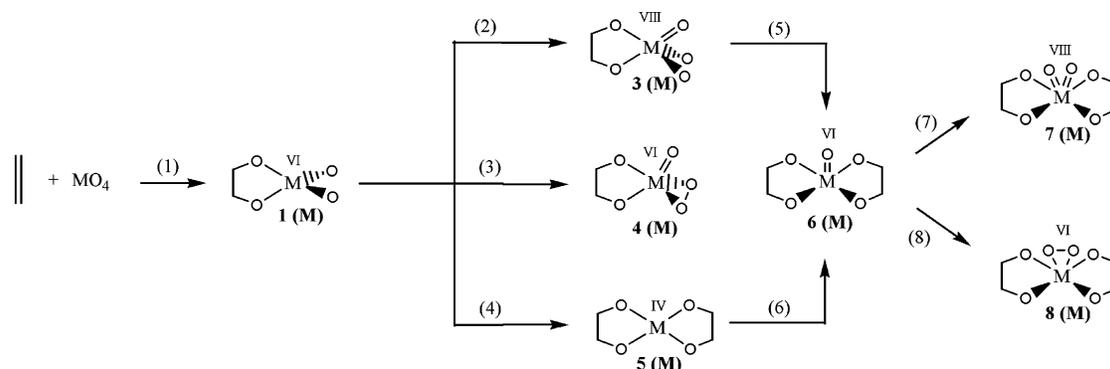


Figure 2. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **1(Ru)** (top) and **1(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

transition states of the reactions have not been calculated in this study, which did not investigate the carbon–carbon bond cleavage step. Systematic experimental studies of the reaction of RuO_4 with olefins have been reported by Sica and co-workers.^{8,10} The Sica group succeeded in isolating and characterizing by NMR spectroscopy for the first time a cyclic ruthenium(VI)diester which is formed during the oxidation reaction.^{10a} Kinetic studies had suggested earlier that the scission

of the carbon–carbon double bond could proceed via formation of a cyclic ruthenium(VI)diester,¹¹ but the mechanism which leads to the formation of the intermediate is not known. In particular, there is no evidence of the species which is the direct precursor for the C–C cleavage reaction. The very scarce knowledge about the mechanism of the oxidation of olefins with RuO_4 becomes obvious from the recent review of Strassner about computational studies of alkene oxidation reactions by metal–oxo compounds.¹²

In this paper, we report a systematic quantum chemical investigation of the oxidation of ethylene with RuO_4 which leads to the scission of the C–C bond. Two questions are addressed in this work. The first question concerns the reaction mechanism of the oxidation. The pivotal aspect in the calculations of viable intermediates and transition states was the search for the precursor species which has a low barrier for the carbon–carbon bond cleavage. The second question concerns the difference between the oxidation reactions of OsO_4 and RuO_4 with olefins. Why is it that the C–C bond is cleaved by RuO_4 but not by OsO_4 ? To this end, we calculated the reaction steps for both metal tetraoxides. It will be seen below that it took much perseverance before a satisfactory answer to both questions was found.

Methods

The geometries have been optimized at the gradient-corrected DFT level using the B3LYP functionals.¹³ A quasi-relativistic small-core ECP with a (441/2111/ N) valence basis set for Ru ($N = 3$) and Os ($N = 2$) and 6-31G(d) basis sets for all other atoms have been employed in the geometry optimizations.¹⁴ This is our standard basis set II.¹⁵ The nature of the stationary points was examined by calculating the Hessian matrix at B3LYP/II. All transition states were connected to their corresponding minima by calculation of the intrinsic reaction coordinate (IRC). The calculations have been carried out with the program package Gaussian 98.¹⁶

- (9) Norrby, P. O.; Kolb, H. C.; Sharpless, K. B. *Organometallics* **1994**, *13*, 344.
- (10) (a) Piccialli, V.; Sica, D.; Smaldone, D. *Tetrahedron Lett.* **1995**, *35*, 7093. (b) Notaro, D.; Piccialli, V.; Sica, D.; Smaldone, D. *Tetrahedron* **1994**, *50*, 4835. (c) Albarella, L.; Lasalvia, M.; Piccialli, V.; Sica, D. *J. Chem. Soc., Perkin Trans.* **1998**, 737. (d) Albarella, L.; Lasalvia, M.; Piccialli, V.; Smaldone, D.; Sica, D. *J. Chem. Res.* **1996**, 400. (e) Albarella, L.; Musumeci, D.; Sica, D. *Eur. J. Org. Chem.* **2001**, 997.
- (11) Lee, D. G.; van den Engh, M. In *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Academic Press: New York, 1973; Vol. 5, Part B, Chapter 4.
- (12) Strassner, T. *Adv. Phys. Org. Chem.* **2003**, *38*, 131.
- (13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. (c) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.
- (14) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

Table 1. Reaction Energies of Metalladioxalanes [kcal/mol], Calculated with B3LYP/II (with Zero-Point Corrections)

Reaction	M=Ru	M=Os
(1) + C ₂ H ₄ →	-64.8 (-60.2)	-32.3 (-27.6)
(2) + H ₂ O ₂ -H ₂ O →	+6.3 (+4.8)	-27.5 (-28.6)
(3) + H ₂ O ₂ -H ₂ O →	-9.2 (-10.5)	-2.0 (-3.3)
(4) + C ₂ H ₄ →	-22.5 (-18.3)	+0.8 (+3.5)
(5) + C ₂ H ₄ →	-96.9 (-91.5)	-62.0 (-56.9)
(6) + H ₂ O ₂ -H ₂ O →	-68.1 (-68.4)	-88.7 (-89.1)
(7) + H ₂ O ₂ -H ₂ O →	+27.7 (+25.4)	-8.7 (-10.2)
(8) + H ₂ O ₂ -H ₂ O →	+4.6 (+2.4)	+20.7 (+18.9)
(9) + ³ [O] →	-12.0 (-11.2)	-48.5 (-46.7)

Results

We first investigated the concerted [3+2] addition of RuO₄ to ethylene and the two-step reaction with initial [2+2] addition and subsequent rearrangement to the metalladioxo-2,5-dioxolane **1**(Ru). Figure 1 shows the calculated reaction profiles for both reactions and a comparison to the OsO₄ reaction which has previously been reported.^{5a} We want to point out that, in our previous investigation, we carried out CCSD(T) calculations which showed that the B3LYP results are in good agreement with the ab initio data.^{5a} The results which are

given in Figure 1 make it obvious that, for both metals, the [3+2] addition is clearly favored over the two-step reaction. The formation of the metalladioxo-2,5-dioxolanes **1**(Ru) and **1**(Os) is in the case of ruthenium significantly more exothermic ($\Delta H^\circ = -60.2$ kcal/mol) than that in the case of osmium (ΔH°

(15) Frenking, G.; Antes, I.; Boehme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, p 63.

(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Milliam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomberts, R.; Martin, R. L.; Fox, D. J.; Keith, T. A.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

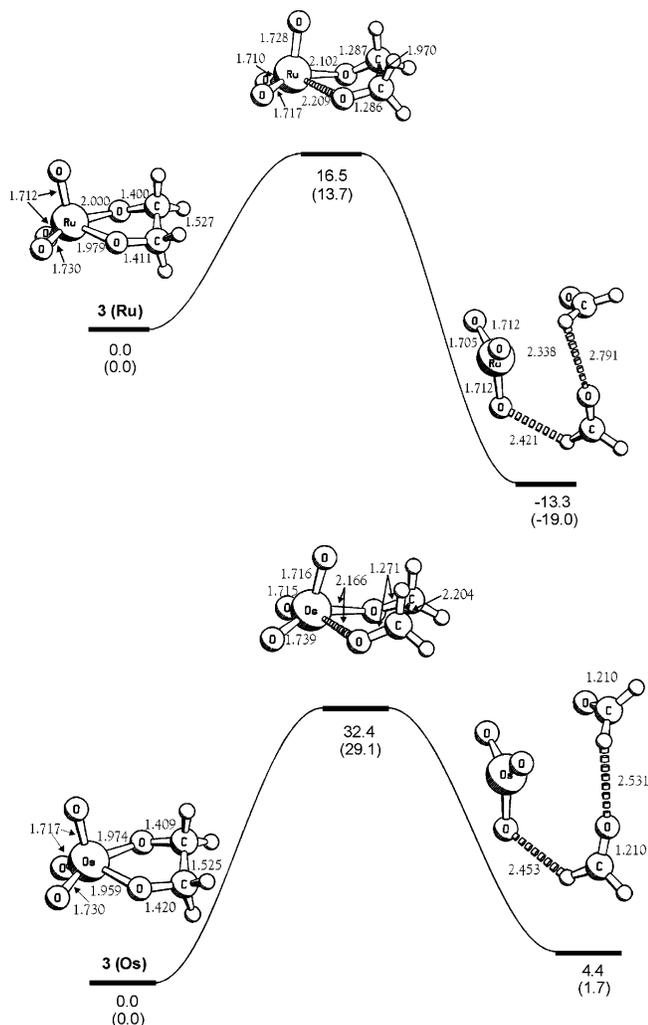


Figure 3. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **3(Ru)** (top) and **3(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

= -27.6 kcal/mol). The activation barrier of the former reaction is also slightly lower ($\Delta H^\ddagger = 5.0$ kcal/mol) than that for the latter ($\Delta H^\ddagger = 6.9$ kcal/mol). The activation energies of the [2+2] addition yielding the metallatrioxo-2-oxetanes **2(Ru)** and **2(Os)** are much higher for RuO_4 ($\Delta H^\ddagger = 43.4$ kcal/mol) and for OsO_4 ($\Delta H^\ddagger = 45.6$ kcal/mol). We conclude that the initial reaction of RuO_4 and OsO_4 to olefins is the concerted [3+2] addition (reaction 1).

The metalladioxo-2,5-dioxolane **1(M)** has been considered as the first intermediate for the C–C bond cleavage yielding two formaldehyde molecules which may be coordinated to the metal dioxide. Figure 2 shows the calculated reaction profile for the direct carbon–carbon cleavage of the metalladioxo-2,5-dioxolanes **1(Ru)** and **1(Os)**. The C–C bond and one metal–oxygen bond are significantly stretched in the transition state structures, yielding a hydrogen-bridged formaldehyde dimer which is coordinated with one oxygen atom to the metal. The reactions for both metals are endothermic. The rather large activation barriers of 46.1 kcal/mol (Ru) and 55.1 kcal/mol (Os) leave no doubt that the direct C–C bond cleavage of **1(Ru)** can be ruled out as the pathway for the oxidation reaction.

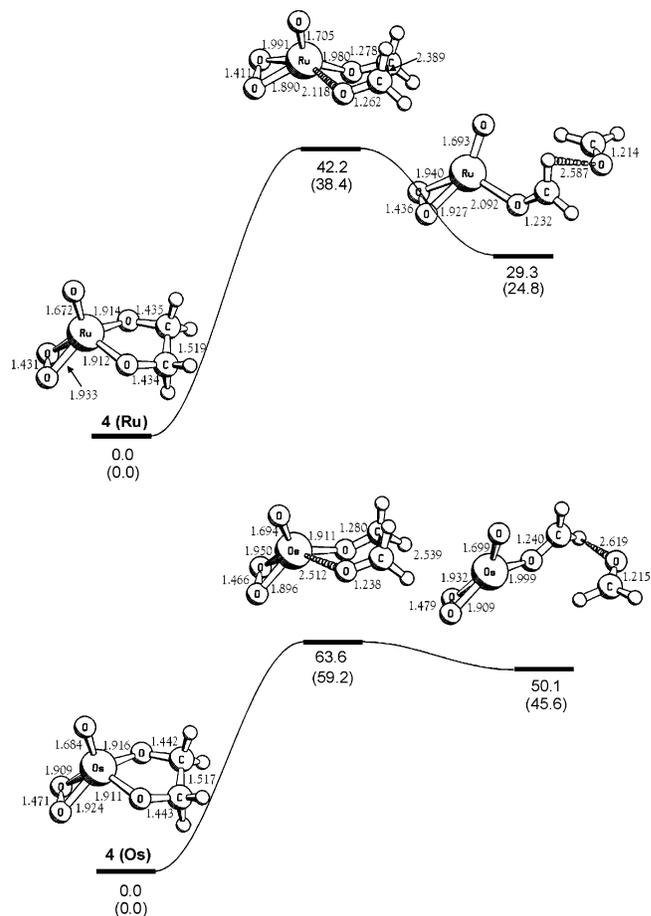


Figure 4. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **4(Ru)** (top) and **4(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

Further reactions of the metalladioxo-2,5-dioxolane **1(Ru)** must be considered in searching for a low-energy C–C bond breaking reaction.

We investigated three possible routes for the further reaction of the metalladioxo-2,5-dioxolane **1(M)** (Scheme 1). The three reaction pathways are the oxidation of the metalladioxo-2,5-dioxolane **1(M)** to the metallatrioxo-2,5-dioxolane **3(M)** (reaction 2), oxidation of **1(M)** to the metalla-oxoperoxo-2,5-dioxolane **4(M)** (reaction 3), and the addition of a second ethylene molecule to **1(M)** yielding the metalla-bis(2,5-dioxolane) **5(M)** (reaction 4).

Table 1 gives the calculated reaction energies for reactions 2–4. The oxidation reactions are assumed to proceed with lower activation barriers than the carbon–carbon cleavage and have therefore been neglected in this work. The choice of H_2O_2 as oxidative agent was made for computational reasons. The calculated values of the oxidation reactions are useful for comparing different reactions and particularly for the comparison of ruthenium with osmium. Stronger oxidants will yield more exothermic (less endothermic) reaction enthalpies. We also neglected a possible activation barrier for the addition reactions of ethylene to the metal oxide species. Calculations of the addition of ethylene to **1(M)** showed that the reaction has a small or even no barrier at all. We think that it is justified for the purpose of this work to consider only the reaction enthalpies of the latter reactions.

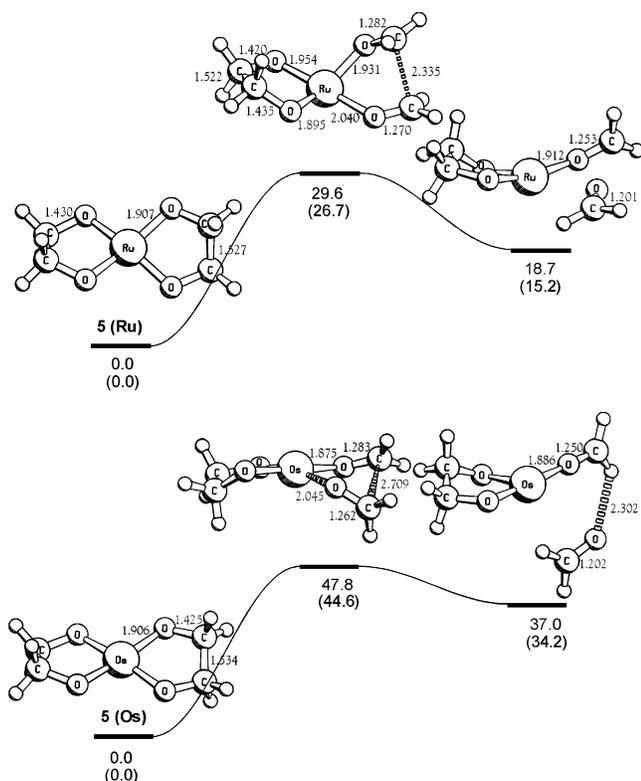


Figure 5. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **5(Ru)** (top) and **5(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

The oxidation reaction 2 is rather exothermic for **1(Os)** ($\Delta H^\circ = -28.6$ kcal/mol) but slightly endothermic for **1(Ru)** ($\Delta H^\circ = 4.8$ kcal/mol). The opposite order is calculated for the addition reaction 4, which is nearly thermoneutral for **1(Os)** ($\Delta H^\circ = 3.5$ kcal/mol) but clearly exothermic for **1(Ru)** ($\Delta H^\circ = -18.3$ kcal/mol). Note that reaction 2 is an oxidation reaction where the formal oxidation state of the metal changes from +6 to +8, while reaction 4 is a reduction where the oxidation state changes from +6 to +4. The oxidation reaction 3 which leaves the metal in the formal oxidation state +6 is slightly exothermic for both metals (-10.5 kcal/mol for Ru and -3.3 kcal/mol for Os). The importance of the formal oxidation state will be discussed below. We want to point out that the addition of ethylene to MO_4 (oxidation state +8) is much more exothermic than the addition reaction to **1(M)** (oxidation state +6; see reactions 1 and 4 in Table 1).

Reactions 2–4 give three intermediates **3(M)**, **4(M)**, and **5(M)**, which are possible candidates for the low barrier C–C bond breaking reaction. The calculated reaction profiles are shown in Figures 3–5. The theoretically predicted activation barriers of all reactions are too high to make them likely candidates for the actual C–C cleavage reaction except for the bond breaking reaction of **3(Ru)** which has an activation barrier of $\Delta H^\ddagger = 13.7$ kcal/mol. Note that the oxidation reaction **1(Ru)** \rightarrow **3(Ru)** is slightly endothermic (Table 1), but a stronger oxidation agent than H_2O_2 could give an exothermic reaction. However, there is a striking argument against a possible role of **3(Ru)** as direct precursor of the carbon–carbon cleavage reaction. Table 1 gives the calculated reaction energies for the formation of the metalla-oxo-bis(2,5-dioxolane) **6(M)** which can

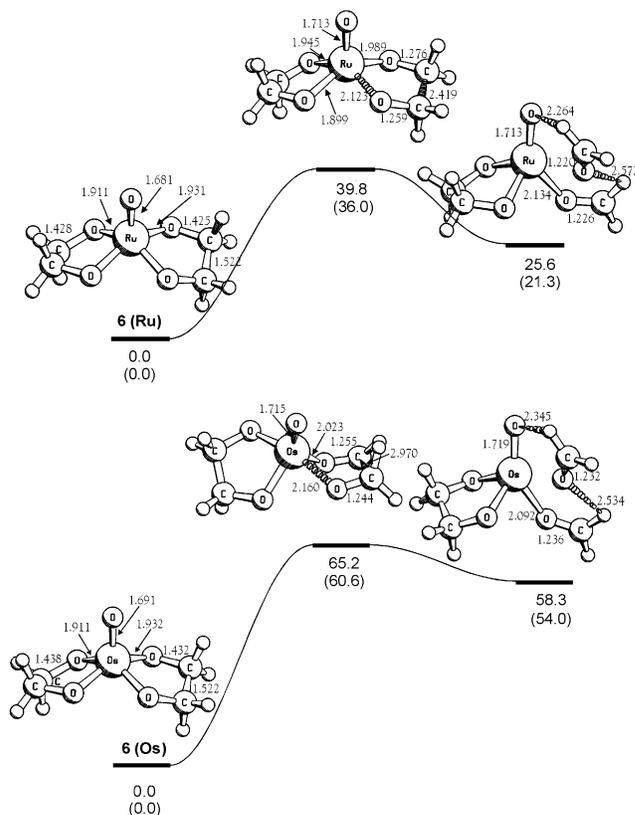


Figure 6. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **6(Ru)** (top) and **6(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

be formed either through addition of ethylene to **3(M)** (reaction 5) or through oxidation of **5(M)** (reaction 6). Both reactions are very exothermic between -56.9 and -91.5 kcal/mol, which makes it unlikely that the intermediates **3(M)** and **5(M)** will be stable in the presence of olefin and oxidizing agent. The calculated reaction energies suggest that metalla-oxo-bis(2,5-dioxolane) **6(M)** should rapidly be formed in the oxidation reaction of olefins with RuO_4 and OsO_4 . The difference between the metals is that **1(Ru)** should first add ethylene yielding **5(Ru)** which is then oxidized to **6(Ru)**, while **1(Os)** is first oxidized to **3(Os)** which then adds another ethylene molecule yielding **6(Os)**. Note that the addition of ethylene to the metal(VIII) species **3(M)** (reaction 5) is much more exothermic than the addition to MO_4 (reaction 1, Table 1).

There is another argument which speaks against the role of **3(Ru)** as a precursor for the C–C cleavage reaction. Table 1 shows that the oxidation of **1(Ru)** would preferably yield the oxoperoxo complex **4(Ru)** (reaction 3) instead of the trioxo species **3(Ru)** (reaction 2). The C–C cleavage reaction of **4(Ru)** has a large activation barrier, however (38.4 kcal/mol, Figure 4).

The conclusion which can be made from the above discussion is that none of the intermediates **3(M)**–**5(M)** is a likely candidate for the low activation energy C–C cleavage reaction which leaves **6(M)** as the next option. Figure 6 shows the calculated reaction profile for the carbon–carbon bond breaking reactions of **6(Ru)** and **6(Os)**. The activation barrier of **6(Ru)** ($\Delta H^\ddagger = 36.0$ kcal/mol) is much lower than that for **6(Os)** ($\Delta H^\ddagger = 60.6$ kcal/mol), but the absolute value of the activation

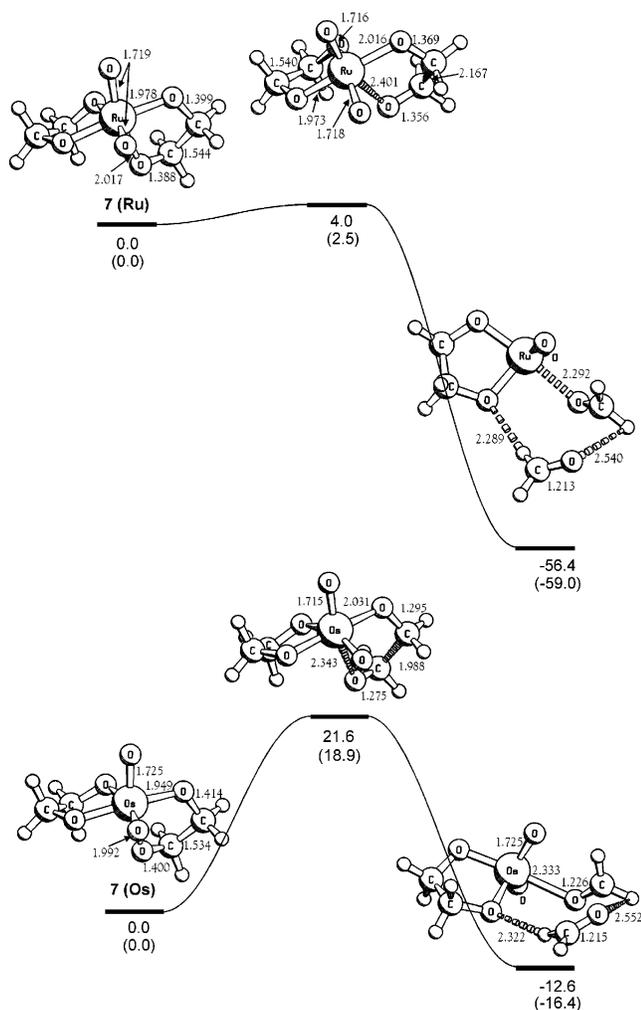


Figure 7. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **7(Ru)** (top) and **7(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

enthalpy is too high to explain the rapid C–C cleavage reaction with RuO_4 . The search for a possible candidate goes on.

Table 1 gives calculated reaction energies for further oxidation reactions of **6(M)** yielding the metalladioxo-bis(2,5-dioxolane) **7(M)** (reaction 7) and the metallaperoxo-bis(2,5-dioxolane) **8(M)** (reaction 8). The reactions are endothermic except for the reaction **6(Os)** \rightarrow **7(Os)** which is -10.2 kcal/mol exothermic. Note, however, that more strongly oxidizing agents than H_2O_2 would make the formation of **7(M)** and **8(M)** more likely. Because the intermediate **7(M)** was found to be particularly important for the C–C bond cleavage reaction (see below), we calculated the reaction energy for the addition of a free oxygen atom in the ^3P electronic ground state to **7(M)** yielding **8(M)** (reaction 9). Table 1 shows that the formation of the Ru(VIII) complex **8(Ru)** is -11.2 kcal/mol exothermic, while the oxidation **7(Os)** \rightarrow **8(Os)** is thermodynamically favored by -46.7 kcal/mol. We want to point out that the calculated energies indicate the thermodynamic potentials of the free molecules which will be influenced in the condensed phase, for example, by coordination of solvent molecules. It has been found experimentally that the oxidation of olefins with RuO_4 in a water/acetone mixture can be tuned toward formation of the *cis*-diol by variation of the temperature.⁸ This may be

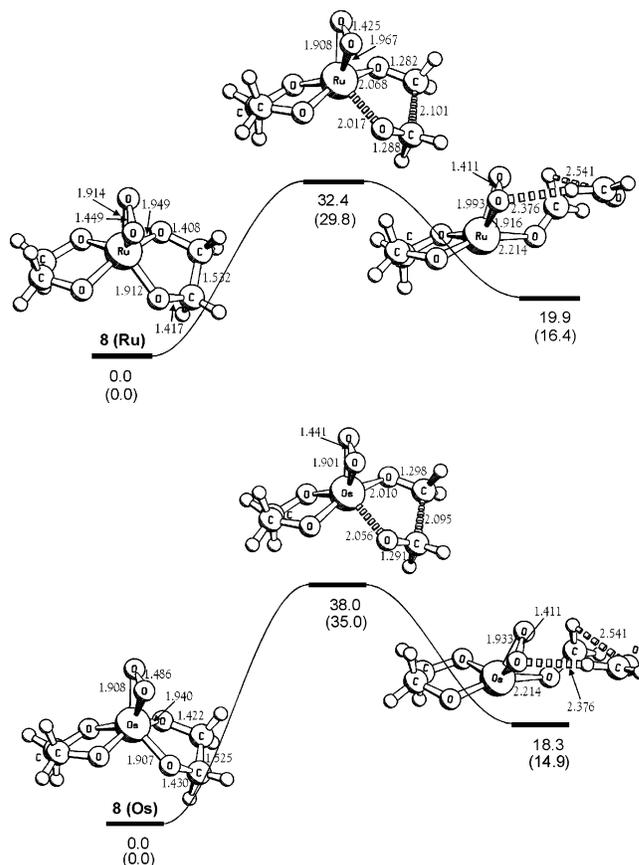


Figure 8. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **8(Ru)** (top) and **8(Os)** (bottom). The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses. The calculated interatomic distances are given in angstroms.

Table 2. Relative Energies [kcal/mol] of the Singlet, Triplet, and Quintet States of Metallabisdioxole **5(M)**, Calculated with B3LYP/II (with Zero-Point Corrections)

configuration of 5(M)	M = Ru	M = Os
singlet	0.0	0.0
triplet	-7.5 (-7.6)	-1.8 (-2.2)
quintet	-5.6 (-6.1)	$+9.9$ ($+9.2$)

explained by the different coordination modes of the complexes at low and high temperatures.

We calculated the C–C cleavage reactions of **7(M)** and **8(M)**. The results are given in Figures 7 and 8.

Figure 7 shows that the metalladioxo-bis(2,5-dioxolane) **7(Ru)** is the first compound in this work which has a very low barrier for the carbon–carbon bond breaking reaction. The theoretically predicted value $\Delta H^\ddagger = 2.5$ kcal/mol is compatible with the experimental observation that the oxidation reaction of olefins at mild conditions proceeds under rupture of the C–C bond.^{7,18} The same reaction of the analogous osmium species **7(Os)** has a significantly higher barrier $\Delta H^\ddagger = 18.9$ kcal/mol which would explain why OsO_4 usually does not break the carbon–carbon bond while RuO_4 does. However, the activation barrier is not prohibitively high to declare a bond cleavage reaction impossible. It is known that under appropriate reaction

(17) (a) Pappo, R.; Allen, D. S., Jr.; Lemieux, R. U.; Johnson, W. S. *J. Org. Chem.* **1956**, *21*, 478. (b) Vorbrüggen, H.; Djerassi, C. *J. Am. Chem. Soc.* **1962**, *84*, 2990.

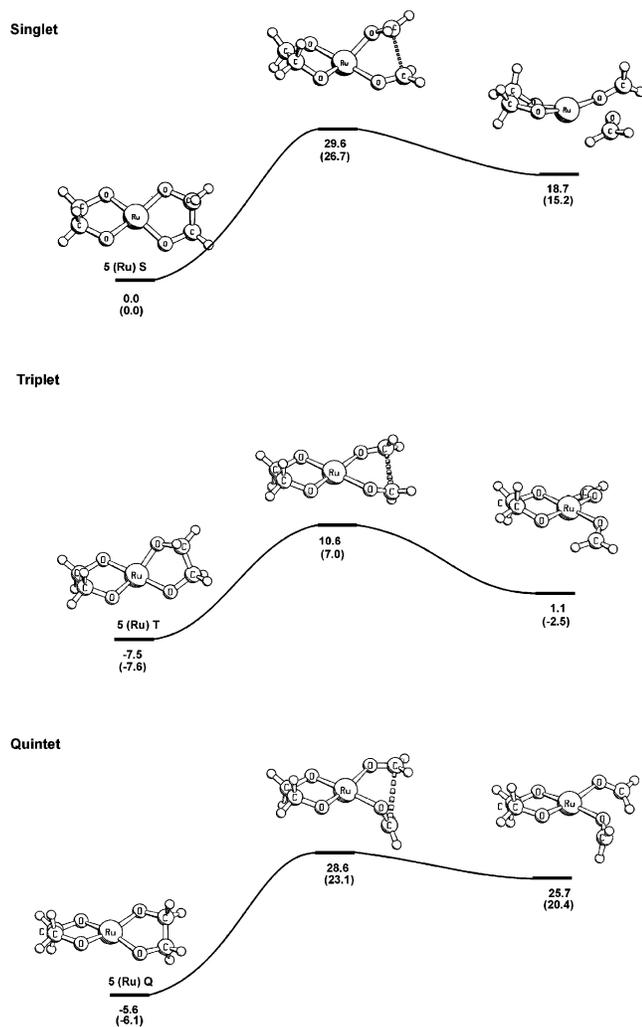


Figure 9. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **5(Ru)** in the lowest lying singlet, triplet, and quintet electronic states. The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses.

conditions and in the presence of a cooxidant, OsO₄ may oxidize olefins under cleavage of the C–C bond.¹⁷ The activation barriers of the C–C cleavage reactions of the metallaperoxybis(2,5-dioxolanes) **8(M)** (Figure 8) are too high to be relevant for the reaction course.

The calculated compounds which have been considered until now have a singlet spin state. It is possible that some transition metal compounds which have a d² or d⁴ configuration of the metal have energetically low-lying triplet or quintet states. We calculated several molecules as open-shell species and found that the metalla-bis(2,5-dioxolane) **5(M)** has energetically low-lying triplet and quintet states which might also be involved in the C–C cleavage reaction. Table 2 gives the relative energies of the lowest lying triplet and quintet state of **5(Ru)** and **5(Os)**. The calculations predict that both molecules have a triplet ground state and that the quintet state of **5(Ru)** is still 6.1 kcal/mol more stable than the singlet state. Figures 9 and 10 display

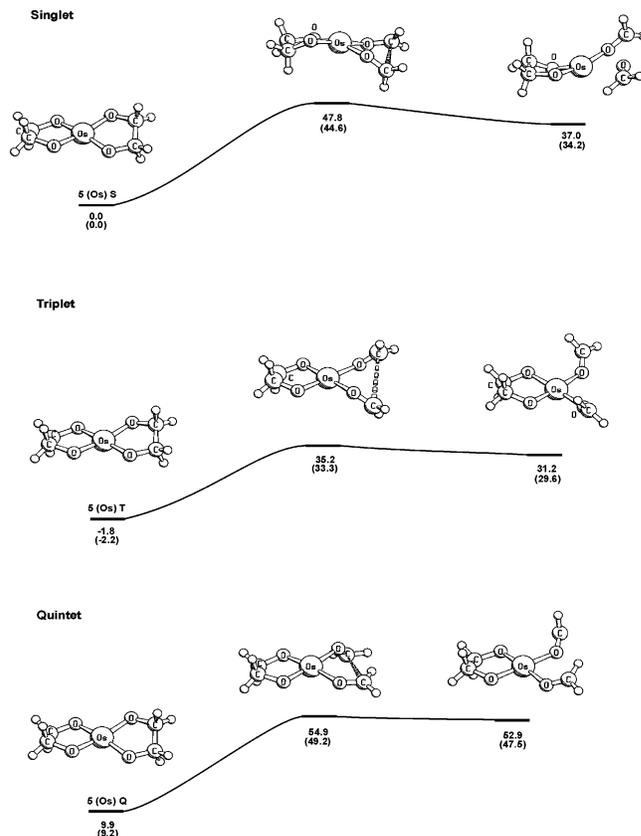


Figure 10. Calculated reaction profiles at B3LYP/II for the C–C bond cleavage reaction of **5(Os)** in the lowest lying singlet, triplet, and quintet electronic states. The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses.

the reaction profiles for the carbon–carbon bond breaking reaction of the singlet, triplet, and quintet states of **5(M)**. The calculations predict that the triplet states have the lowest activation barriers for the C–C bond rupture. The calculated activation barriers with respect to the triplet states of **5(M)** are $\Delta H^\ddagger = 14.6$ kcal/mol for **5(Ru)** and $\Delta H^\ddagger = 31.1$ kcal/mol for **5(Os)**. Although the activation barrier for the triplet state of **5(Ru)** is not very high, it is significantly higher than the activation energy of the singlet state of **7(Ru)**. Therefore, we think that the C–C bond breaking step of the olefin oxidation with RuO₄ takes place after **7(Ru)** is formed which is the direct precursor of the carbonyl compounds. A possible alternative would be that the singlet–triplet conversion of **5(Ru)** is very fast, conserving the internal energy of singlet **5(Ru)** which would then require an activation energy of only 7.0 kcal/mol (Figure 9). We think that the latter reaction pathway is less likely (but cannot be ruled out) because the reaction takes place in a condensed phase where the internal energy of singlet **5(Ru)** is quickly released, and because the oxidation reaction **5(Ru)** → **6(Ru)** is a highly exothermic process (Table 1) which will occur very fast.

Figures 11 and 12 display the calculated reaction steps for the oxidation of ethylene with RuO₄ and OsO₄. The calculations suggest that the multiple-step oxidation with ruthenium tetraoxide (Figure 11) takes place with the sequential formation of the intermediates **1(Ru)** → **5(Ru)** → **6(Ru)** → **7(Ru)** → C–C bond cleavage. The oxidation with osmium tetraoxide (Figure 12) exhibits the intermediates **1(Os)** → **3(Os)** → **6(Os)** → **7(Os)**, but the cleavage of the carbon–carbon bond of **7(Os)** is clearly

(18) (a) Haines, A. H. *Methods for the Oxidation of Organic Compounds*; Academic Press: London, 1985. (b) Courtney, J. L. In *Organic Syntheses by Oxidation with Metal Compounds*; Mijs, W. J., de Jonge, C. R. H. I., Eds.; Plenum Press: New York, 1986; Chapter 8. (c) Lee, D. G.; Chen, T. In *Cleavage Reactions in Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 7, p 541.

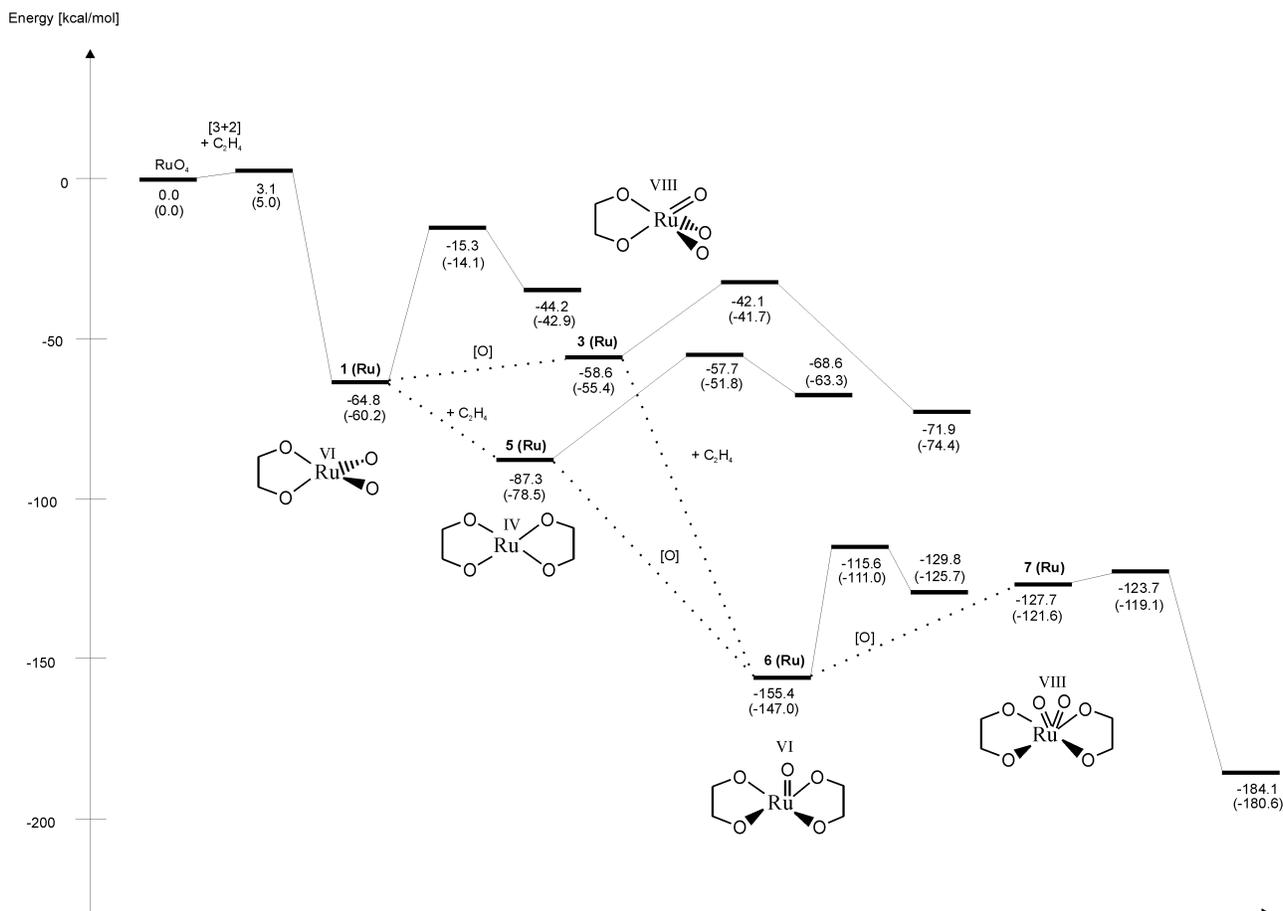


Figure 11. Calculated overall reaction profile at B3LYP/II for the reaction of RuO_4 with ethylene. The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses.

higher than for $7(\text{Ru})$. The formation of the intermediates $6(\text{Os})$ and $7(\text{Os})$ has been postulated by Sharpless who suggested that two reaction cycles are competing in the catalytic dihydroxylation of olefins.¹⁹ According to Sharpless, one reaction cycle which proceeds with low enantioselectivity starts with the formation of $3(\text{Os})$ which is stabilized with a chiral ligand L. Substitution of L by an olefin yields $6(\text{Os})$ which is then oxidized to $7(\text{Os})$. The latter species is partially hydrolyzed, yielding a *cis*-diol and $3(\text{Os})$ which becomes stabilized again by L, closing the second reaction cycle. The calculated reaction course shown in Figure 12 supports the postulated mechanism of Sharpless. Our calculations predict that the ruthenium system exhibits the same reaction cycle except that $7(\text{Ru})$ undergoes C–C bond scission instead of hydrolysis.

We want to point out that compound $6(\text{Os})$ has been isolated and an X-ray structure analysis of the molecule has been published.²⁰ The theoretically predicted bond lengths and angles which are presented here and in a previous theoretical study which reported Hartree–Fock geometries are in very good agreement with the experimental data.²¹

Why is the activation barrier for the C–C cleavage reaction of $7(\text{Ru})$ so low whereas the activation energy of $7(\text{Os})$ is much higher? The different behavior of the ruthenium and osmium compounds can be explained by the propensity of the metals to be in a high oxidation state. It is well known that osmium compounds which have a high oxidation state of the metal are

more stable than the respective ruthenium compound. A comparison of the calculated reaction energies which are given in Table 1 shows that reactions 2, 6, 7, and 9 which increase the oxidation state of the metal are in the case of $\text{M} = \text{Os}$ much more exothermic than for $\text{M} = \text{Ru}$. The opposite order is calculated for reactions 1, 4, and 5 where the oxidation state of the metal becomes less. The latter reaction for $\text{M} = \text{Ru}$ is clearly more exothermic than that for $\text{M} = \text{Os}$.

Examination of Figures 1–12 shows that the larger propensity of Os for high oxidation states also becomes manifest in the calculated activation barriers. Reactions where the oxidation state of the metal increases have larger activation barriers for $\text{M} = \text{Ru}$ than for $\text{M} = \text{Os}$, while reactions which reduce the oxidation state have a lower activation barrier for ruthenium compounds. Figure 6 gives a striking example. The C–C bond breaking reaction of $6(\text{M})$ changes the oxidation state from +6 to +4. The reaction of $6(\text{Os})$ is 54.0 kcal/mol endothermic and has an activation barrier of $\Delta H^\ddagger = 60.6$ kcal/mol, while the reaction of $6(\text{Ru})$ is only 21.3 kcal/mol endothermic and has an activation barrier of only $\Delta H^\ddagger = 36.0$ kcal/mol. The very low activation barrier $\Delta H^\ddagger = 2.5$ kcal/mol for the C–C bond cleavage reaction of $7(\text{Ru})$ can be explained with the driving force which comes from lowering the oxidation state Ru(VIII) to Ru(VI). The question of why olefins are oxidized by RuO_4 under cleavage of the carbon–carbon bond whereas oxidation by OsO_4 yields *cis*-diols can thus be answered with the

(19) Wai, J. S. M.; Markó, I.; Svendsen, J. S.; Finn, M. G.; Jacobsen, E. N.; Sharpless, K. B. *J. Am. Chem. Soc.* **1989**, *111*, 1123.

(20) Phillips, F. L.; Skapski, A. C. *Acta Crystallogr.* **1975**, *B31*, 1814.

(21) Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 4937.

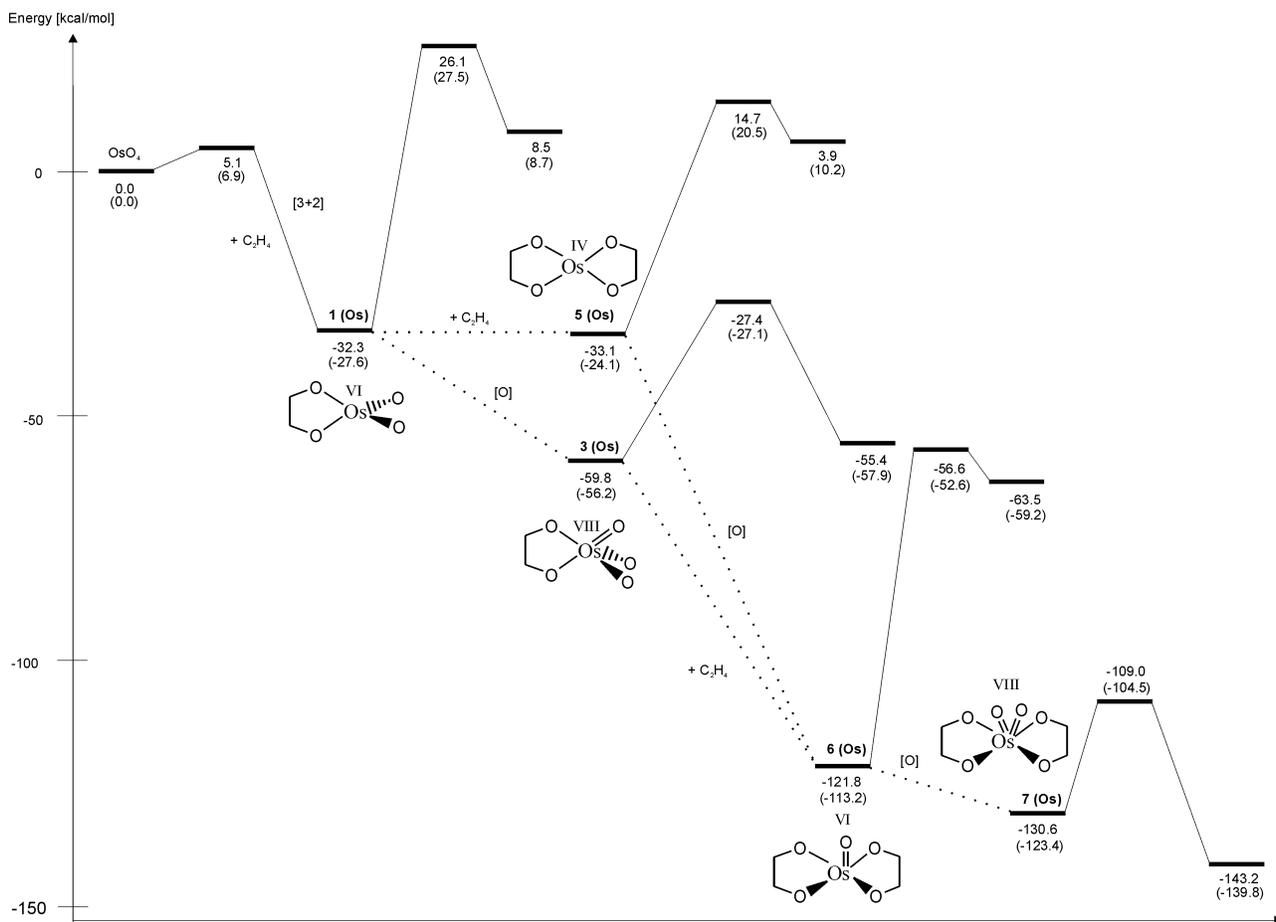


Figure 12. Calculated overall reaction profile at B3LYP/II for the reaction of OsO_4 with ethylene. The energy values are given in kcal/mol, and the ZPE-corrected values are given in parentheses.

significantly lower stability of Ru(VIII) compounds as compared to that of Os(VIII) compounds.

Summary

The results of this work can be summarized as follows. The calculated reaction profiles for the addition of RuO_4 and OsO_4 to ethylene indicate that, for both metal tetraoxides, the concerted [3+2] cycloaddition has much lower activation barriers than the [2+2] addition and the following rearrangement to the metalladioxo-2,5-dioxolane **1(M)**. The C–C bond cleavage reaction of **1(M)** has high activation barriers for $M = \text{Ru}$ and $M = \text{Os}$ and may not be considered as a precursor for the oxidation of olefins with RuO_4 yielding carbonyl compounds. The calculations suggest that **1(Ru)** reacts exothermically with another ethylene molecule in a second [3+2] addition yielding the metalla-bis(2,5-dioxolane) **5(Ru)**, while **1(Os)** is further oxidized to the metallatrioxo-2,5-dioxolane **3(Os)**. The latter species reacts strongly exothermically with ethylene toward formation of the energetically very low-lying metalla-oxo-bis(2,5-dioxolane) **6(Os)**. The ruthenium compound **6(Ru)** should be formed during the reaction course through oxidation of **5(Ru)**. The initial addition product **1(M)** may also become oxidized to the metalla-oxoperoxo-2,5-dioxolane **4(M)** in a weakly exothermic reaction. However, the activation barriers of the C–C bond cleavage reactions of **3(Ru)**, **4(Ru)**, **5(Ru)**, and **6(Ru)** are too high to explain the rapid oxidation of olefins with RuO_4 yielding carbonyl compounds. The activation barriers of the respective osmium compounds are higher than those for the ruthenium

species. Further oxidation of **6(M)** toward formation of the metalladioxo-bis(2,5-dioxolane) **7(M)** or the metalla-peroxo-bis(2,5-dioxolane) **8(M)** is energetically less favorable than the previous reactions. However, the ruthenium compound **7(Ru)** has a very low activation barrier of $\Delta H^\ddagger = 2.5$ kcal/mol which is compatible with the experimental observation that the oxidation reaction of olefins at mild conditions proceeds under rupture of the C–C bond. The activation barrier of **7(Os)**, $\Delta H^\ddagger = 18.9$ kcal/mol, is higher which explains why RuO_4 but not OsO_4 cleaves the C–C bond of olefins. Calculations of the intermediates in higher spin states show that the triplet and quintet states of **5(Ru)** and the triplet state of **5(Os)** are lower in energy than the singlet state. However, the activation barriers for the C–C cleavage reactions of the triplet and quintet states of **5(M)** are significantly higher than the activation barriers of the singlet state. The theoretical results of this work suggest that the oxidation of olefins with RuO_4 which cleaves the C–C bond takes place via formation of **7(Ru)** as the precursor intermediate. The different reactivity between OsO_4 and RuO_4 is explained by the higher stability of Os(VIII) as compared to that of Ru(VIII) compounds. The calculated energies show that reactions where the oxidation state of the metal increases have larger activation barriers for $M = \text{Ru}$ than for $M = \text{Os}$, while reactions which reduce the oxidation state have a lower activation barrier for ruthenium compounds. Also, reactions which increase the oxidation state of the metal are in the case of $M = \text{Os}$ more exothermic than for $M = \text{Ru}$.

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