

## THE MECHANISM OF THE PERMANGANATE-PROMOTED OXIDATIVE CYCLIZATION OF 1,5-DIENES – A DFT STUDY

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*Dedicated to Dr Karel Mach on the occasion of his 70th birthday in recognition of his outstanding contributions to the area of organometallic synthesis and catalysis.*

The mechanism of the permanganate oxidation of 1,5-dienes was investigated by density functional theory calculations (B3LYP/6-311+G\*). The experimentally observed (unexpected) products, 2,5-bis(hydroxymethyl) tetrahydrofurans, are formed in a concerted reaction, which explains the observed stereoselectivity of the reaction. Water plays an important role in the reaction mechanism by significantly lowering the activation energies.

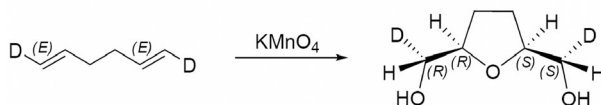
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The oxidation of alkenes can be accomplished with a variety of metal-oxo compounds like OsO<sub>4</sub>, RuO<sub>4</sub> or KMnO<sub>4</sub> and has been known for quite some time<sup>1-6</sup>. Permanganate is known to oxidize alkenes to diols or even further by breaking the C–C bond<sup>7-11</sup>. Mechanistic aspects of the oxidations have been studied in great detail, also in combination with kinetic isotope effects<sup>12-30</sup>.

In 1965 the permanganate-promoted oxidation of 1,5-dienes was investigated by Klein and Rojahn<sup>31</sup>, who wanted to explain the unexpected formation of 2,5-bis(hydroxymethyl) tetrahydrofurans with defined stereochemistry instead of tetroles, as was initially claimed by Wagner<sup>8</sup> and Boeseken<sup>32</sup>. It was reported that this reaction could also be performed by using other metal-oxo compounds like ruthenium tetroxide, perrhenate and osmium tetroxide<sup>33-41</sup>. Baldwin et al.<sup>42</sup> confirmed the stereospecific course of the reaction using deuterium-labeled 1,5-dienes (Scheme 1).

Due to the stereospecific formation of up to four new stereogenic centers and the THF ring, this reaction is a valuable tool for the synthesis of this

important structural unit of several biologically active molecules<sup>43-47</sup>. The use of chiral auxiliaries<sup>48,49</sup> and phase-transfer permanganate-promoted oxycyclization<sup>50</sup> has already been shown to provide enantiomerically enriched THF diols.



SCHEME 1  
Baldwin's experiment<sup>42</sup>

Based on their experimental evidence, Klein and Rojahn<sup>31</sup> proposed the concerted formation of a complex between the two double bonds of the 1,5-diene and the permanganate (Fig. 1).

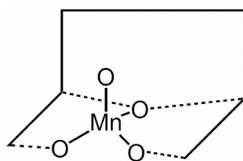


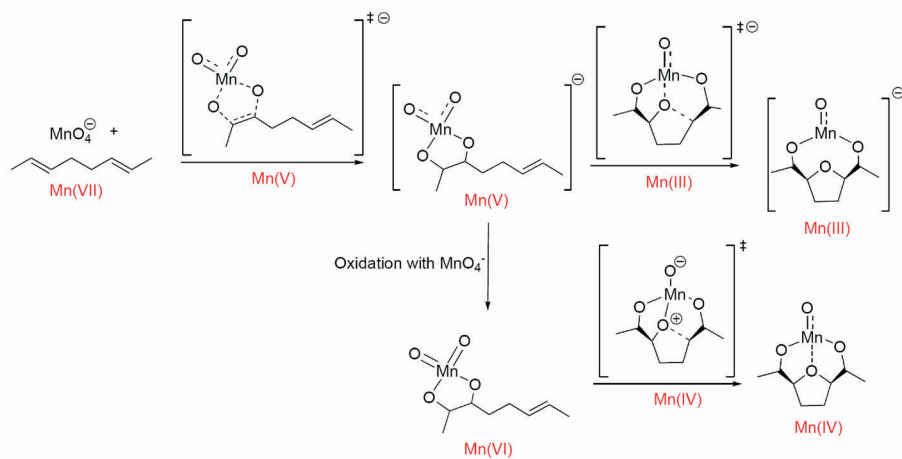
FIG. 1  
Concerted formation of a permanganate-diene complex proposed by Klein and Rojahn<sup>31</sup>

For a similar reaction including permanganate ions, a stepwise mechanism was proposed by Sable et al.<sup>51</sup>, which was adopted for the reaction with 1,5-dienes by Wolfe and Ingold<sup>52</sup>, supported by the confirmation of the existence of the intermediate manganese(V) ester.

A comproportionation of the manganese(V) ester with another permanganate molecule forming a manganese(VI) ester and manganate(VI) was also suggested<sup>42</sup>, since there was experimental evidence that the manganese(V) species  $\text{MnO}_4^{3-}$  was not able to oxidize carbon-carbon double bonds<sup>53</sup>, while electron transfer from manganese(V) to the permanganate ion seemed more likely to happen<sup>54</sup>.

Wolfe and Ingold<sup>52</sup> furthermore reported evidence for a possible involvement of water molecules in the mechanism by performing oxygen labeling experiments. There is general agreement on the first reaction step, the formation of the manganese(V) ester. The mechanism is consistent with the

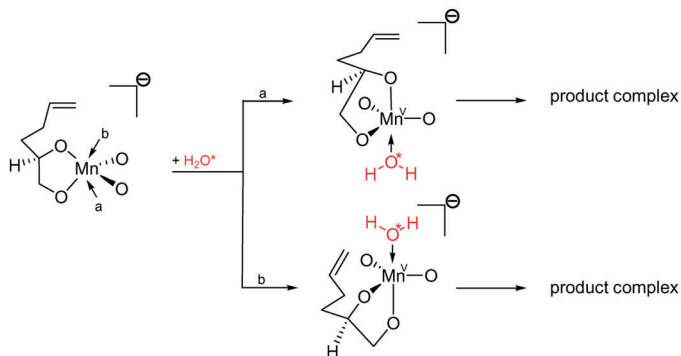
[3+2] reaction pathway described below (Scheme 2). The [2+2] reaction pathway suggested by Walba<sup>55</sup> has been shown to be unreasonably high in energy by thorough mechanistic investigations<sup>21</sup>.



SCHEME 2

Possible reaction paths:  $\text{Mn(VII)} \rightarrow \text{Mn(V)} \rightarrow \text{Mn(III)}$  and  $\text{Mn(VII)} \rightarrow \text{Mn(V)} \rightarrow \text{Mn(VI)} \rightarrow \text{Mn(IV)}$  (including a comproportionation with an additional permanganate ion)

Starting from this intermediate Wolfe and Ingold<sup>52</sup> suggested the addition of a water molecule to the manganese(V) ester, leading to a manganese species with a coordination number greater than four (Scheme 3) which allows exchange of the oxygen atoms before reacting with the second double bond forming the product complex.



SCHEME 3

Addition of an  $\text{O}^{18}$ -labeled water molecule ( $\text{H}_2\text{O}^*$ ) to the manganese(V) ester as suggested by Wolfe and Ingold<sup>52</sup>

Out of the three oxygen atoms in the product, two and a half were found to come from the permanganate ion and the other half from the solvent<sup>52</sup>. However, due to the uncertainty of possible oxygen scrambling and/or interconversion of the possible manganese complexes, they did not suggest a detailed structure of the intermediate.

By applying modern quantum chemical methods, we are able to propose a plausible reaction path and to confirm or disprove the proposed mechanisms suggested earlier. During the last decade, the possibility of a two-state reactivity<sup>56</sup> was also reported for permanganate<sup>22,24</sup>. We were therefore carefully evaluating the accessible potential energy hypersurfaces (PES) for all possible multiplicities, but did not attempt to identify the crossing points between the potential energy hypersurfaces.

### COMPUTATIONAL DETAILS

All calculations were performed with Gaussian03<sup>57</sup>, using the density functional/Hartree–Fock hybrid model Becke3LYP<sup>58–61</sup> and the split valence triple- $\zeta$  (TZ) basis set 6-311+G(d)<sup>62–69</sup> for C, H, O and Mn. Though B3LYP might overestimate higher multiplicities because the energy splittings between low-spin and high-spin are strongly dependent on the exact exchange admixture parameter, in general it is an advisable functional and, in average, works well<sup>70,71</sup>.

No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as being true minima by the absence of negative eigenvalues in the vibrational frequency analysis. Transition-state structures (indicated by TS) were located using the Berny algorithm<sup>72</sup> until the Hessian matrix had only one imaginary eigenvalue. The identities of all transition states were checked by animating the negative eigenvector coordinate with MOLDEN<sup>73</sup> and GaussView, for selected transition states by IRC calculations.

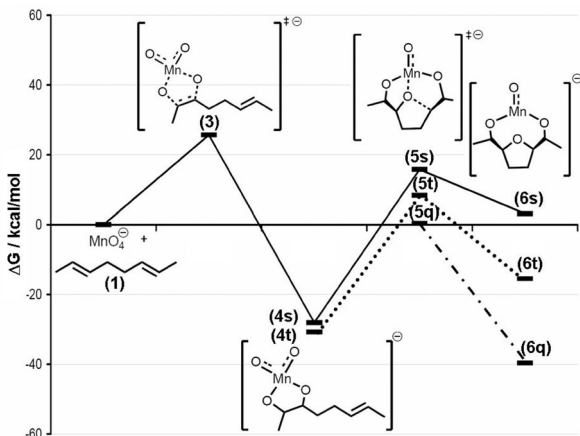
The results are shown for the different potential energy hypersurfaces (PES), as referred to in the text. Approximate Gibbs free energies ( $\Delta G$ ) and enthalpies ( $\Delta H$ ) were obtained through thermochemical analysis by frequency calculations, using the thermal correction to the Gibbs free energy as reported by Gaussian03. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are Gibbs free energies or enthalpies at 298 K, using unscaled frequencies. They are given relative to the combined energy of the starting materials. All transition states are maxima on the electronic poten-

tial energy hypersurface, which may not correspond to maxima on the free energy surface.

## RESULTS AND DISCUSSION

First we examined the simplest mechanism possible for the oxidation of octa-2,6-diene **1** by permanganate **2** on the singlet potential energy surface (PES) as shown in Scheme 4. According to our calculations and in agreement with the experimental results, the formation of the intermediate manganese(V) ester **4** is exergonic ( $\Delta G = -28.1$  kcal/mol) and proceeds via transition state **3** with an activation barrier of 25.6 kcal/mol. From our previous experience<sup>22,24</sup> we can exclude a triplet transition state for the first reaction step, but, starting with intermediate **4**, more potential energy hypersurfaces are accessible. On the singlet potential energy surface (PES), the reaction step from **4s** to **6s** via transition state **5s** is endergonic by  $\Delta G = +31.2$  kcal/mol with an activation barrier of 43.8 kcal/mol.

We also checked whether another possible intermediate exists, connecting **4s** and **6s** with one oxygen atom already attached to the second double bond, but did not find any. An intrinsic reaction coordinate (IRC) simulation starting from transition state **5** was performed which led to intermediates **4** and **6**, supporting the mechanism without an additional intermediate.



Scheme 4

Reaction path Mn(VII)  $\rightarrow$  Mn(V)  $\rightarrow$  Mn(III) with the singlet (—), triplet (· · ·) and quintet (- · -) potential energy surfaces

According to our calculations the triplet surface is easily accessible to intermediate **4**. While the energy for intermediate **4t** is only 2.7 kcal/mol lower than **4s**, that of the triplet product **6t** is favored by 18.6 kcal/mol compared to **6s**. As can be seen from Scheme 4, the barrier for **5t** is also significantly lowered compared to **5s**.

Since the necessary criteria for a crossing point are sufficiently similar energies as well as similar geometries, we predict that the crossing point between the singlet and triplet PES is around intermediate **4**. The two geometries of **4s** and **4t** are shown in Fig. 2.

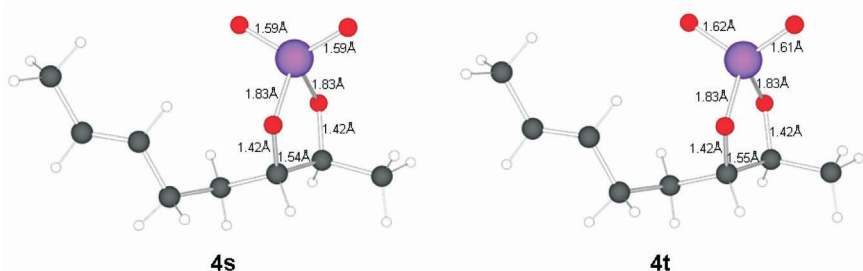


FIG. 2  
Intermediates **4s**, **4t**

Nevertheless, the second reaction step still would be endergonic by +15.2 kcal/mol with an activation barrier of 39.1 kcal/mol, although the overall reaction would be exergonic ( $\Delta G^{\text{total}} = -15.5$  kcal/mol).

We therefore checked the quintet surface, where the transition state **5q** and the product **6q** are calculated to have the lowest barrier as well as the largest product stabilization energy. Relative to intermediate **4t**, a barrier of +31.1 kcal/mol and an exergonic reaction by -9.0 kcal/mol were calculated. For the overall reaction a total Gibbs free energy ( $\Delta G^{\text{total}}$ ) of -39.7 kcal/mol was found. Therefore, another crossing point of the triplet and quintet PES is most likely located between the triplet intermediate **4t** and the quintet transition state **5q**.

A comparison of the geometries of the transition states **5** and the products **6** on the different potential energy surfaces shows an elongation of the central Mn-O<sub>THF</sub> bond with increasing multiplicity. As this result by itself is not surprising, the magnitude of the change from 2.05 Å (**6s**) to 2.59 Å (**6q**) is unexpected.

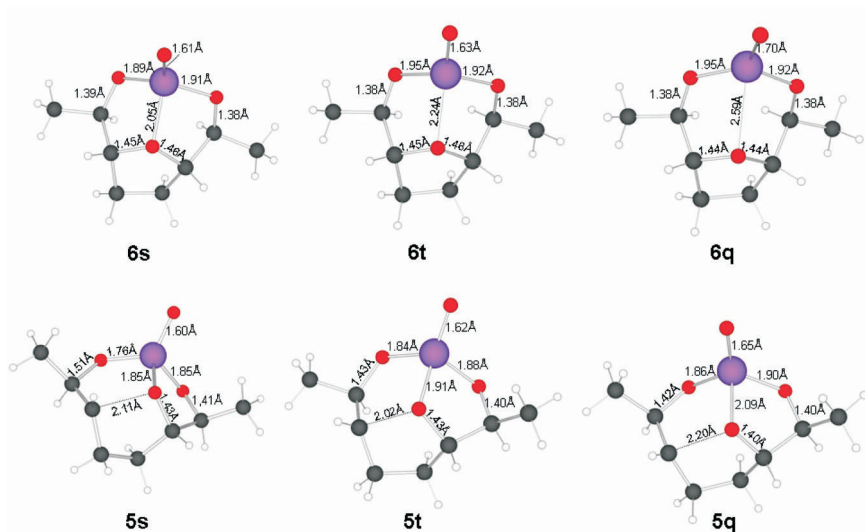


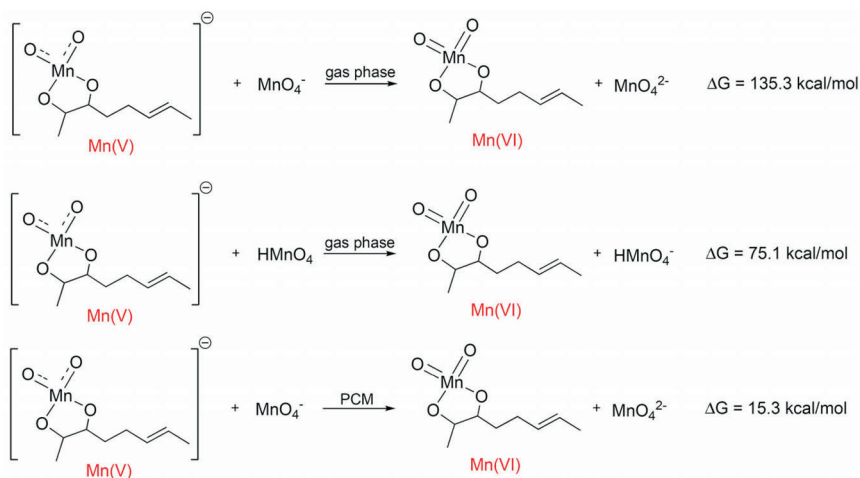
FIG. 3 Selected bond lengths of transition states **5s**, **5t** and **5q** as well as of the products **6s**, **6t** and **6q**

The literature agrees on the first reaction step, but proposed several different pathways from there, which will be discussed separately in the following section.

### *Electron Transfer*

Baldwin proposed a mechanism involving a one-electron transfer from the manganese(V) ester to another permanganate ion leading to a Mn(VI) species on the dublet PES by comproportionation with an additional permanganate ion (Scheme 5). To evaluate the probability of this proposal, we calculated the Gibbs free energy of the formation of the Mn(VI) species, using different approaches. First we calculated the Gibbs free energy for this transformation in the gas phase. The resulting Gibbs free energy (+135.3 kcal/mol) is extremely high, but not surprising, since a dianion and a neutral species are formed from two monoanions. Additionally we applied a PCM solvent model and calculated a charge neutral process using  $\text{HMnO}_4$ . The comproportionation between a monoanion (manganese(V) ester) and a neutral species ( $\text{HMnO}_4$ ) results in the formation of another monoanion (protonated manganate(VI)) and a neutral species (manganese(VI) ester). This drastically lowered the calculated Gibbs free energy for the reaction to 75.1 kcal/mol.

Application of the PCM solvent model using water as the solvent is still unfavorable by 15.3 kcal/mol. We can conclude that all calculations lead to an endergonic intermediate. Therefore, we considered this transformation unlikely to happen and did not further examine this pathway (Scheme 5).



SCHEME 5

Comproportionation of the Mn(V) species with permanganate

### Addition of Water

Starting from structure **4** we also calculated the addition of water molecules to the manganese(V) ester. Various possibilities how the water molecule can add to the manganese(V) ester were considered and the structure with the lowest energy was used for the calculations. The optimizations led to structures where one proton migrated to a permanganate oxygen atom.

On the singlet surface, the addition of the water molecule ( $\mathbf{4s} \rightarrow \mathbf{4}_s^{\text{H}_2\text{O}}$  /  $\mathbf{4t} \rightarrow \mathbf{4}_t^{\text{H}_2\text{O}}$ ) with a Gibbs free energy of 3.7 kcal/mol is a nearly thermo-neutral process. An equilibrium prior to the following addition of the manganese(V) ester to the second double bond seems likely. Due to this equilibrium between **4** and  $\mathbf{4}^{\text{H}_2\text{O}}$  (for singlet and triplet surface), an exchange of the oxygen atoms is possible, which would explain the results of Wolfe and Ingold<sup>52</sup>.

The addition of a second water molecule leading to complex  $\mathbf{4}_s^{2\text{H}_2\text{O}}$  is thermodynamically disfavored by a Gibbs free energy difference of +18.6 kcal/mol compared to  $\mathbf{4}_s^{\text{H}_2\text{O}}$ . With the probable crossing from  $\mathbf{4}_s^{\text{H}_2\text{O}}$  to

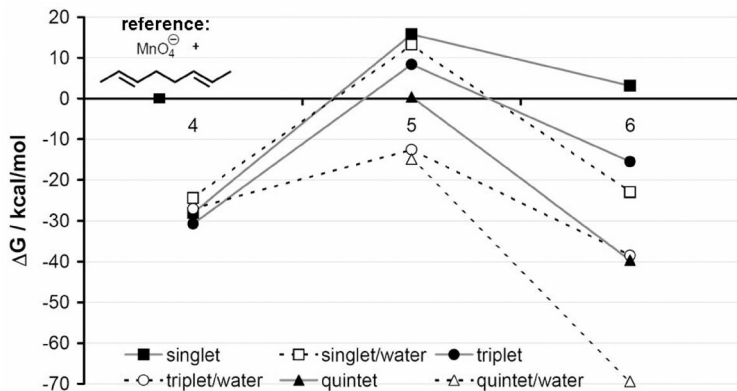


the triplet surface  $4_t^{\text{H}_2\text{O}}$ , the activation barrier between  $4_t^{\text{H}_2\text{O}}$  and  $5_t^{\text{H}_2\text{O}}$  is only 14.5 kcal/mol, so this should be the preferred reaction pathway. This also agrees with the results of Wolfe and Ingold<sup>52</sup>, whose experiments were inconsistent with the addition of a second water molecule.

Our calculations show an increasing stabilization of the molecules during the reaction, if one water molecule remains in the complex. The stabilization energy due to the water addition is given as  $\Delta\Delta G$  in Table I.

Due to the transfer of one water hydrogen to a permanganate oxygen, there are two possibilities for the second transition state  $5^{\text{H}_2\text{O}}$ , either by interaction of a hydroxyl-like oxygen or an oxo-oxygen with the second double bond. On the singlet surface we found a lower activation barrier for the unsubstituted oxygen ( $5_s^{\text{H}_2\text{O}}$ ).

The trends of the reaction energies are similar with and without water, higher multiplicities resulting in lower energies (Scheme 6).



SCHEME 6

Reaction path Mn(VII)  $\rightarrow$  Mn(V)  $\rightarrow$  Mn(III) with (---) and without (—) an added water molecule.  $\Delta G = 0$  kcal/mol refers to the energy of the starting material

A crossing between the singlet and triplet PES followed by the addition of the water molecule is likely. The quintet surface shows the lowest energies for transition state  $5_q^{\text{H}_2\text{O}}$  and product  $6_q^{\text{H}_2\text{O}}$ . Therefore, another crossing from the triplet to the quintet PES leads to the lowest activation barrier of 12.1 kcal/mol ( $4_t^{\text{H}_2\text{O}} \rightarrow 5_q^{\text{H}_2\text{O}}$ ) and an overall total energy of -42.4 kcal/mol ( $4_t^{\text{H}_2\text{O}} \rightarrow 6_q^{\text{H}_2\text{O}}$ ).

A possible reason for the stabilization of the transition state by water could be the coordination geometry around the manganese. Because of the added water molecule in transition state  $5_q^{\text{H}_2\text{O}}$ , its coordination can be de-

TABLE I  
Thermodynamic data for all calculated structures and stabilization effects due to the addition of a water molecule (s, singlet ; t, triplet; q, quintet structures)

Structure	Without water			With water			Stabilization $\Delta\Delta G$ kcal/mol
	$\Delta H$ kcal/mol	$\Delta G$ kcal/mol	$\Delta S$ cal/(K mol)	$\Delta H$ kcal/mol	$\Delta G$ kcal/mol	$\Delta S$ cal/(K mol)	
(1+2)	0.0	0.0	0.0	-	-	-	-
3	12.2	25.6	-44.9	-	-	-	-
4s	-41.7	-28.1	-45.7	-49.7	-24.4	-85.1	3.7
4t	-43.4	-30.7	-42.6	-51.2	-27.0	-81.2	3.7
5s	-2.1	15.8	-60.0	-15.3	13.2	-95.7	-2.6
5t	-7.6	8.4	-53.7	-40.7	-12.5	-94.5	-20.9
5q	-15.2	0.4	-52.2	-42.1	-14.9	-91.4	-15.3
6s	-13.4	3.1	-55.3	-50.8	-23.0	-93.3	-26.1
6t	-30.9	-15.5	-51.7	-64.9	-38.5	-88.7	-23.0
6q	-54.6	-39.7	-50.0	-95.9	-69.4	-88.8	-29.7

scribed as trigonal bipyramidal, which is in general preferred by manganese(V) compounds. The coordination environment of the product  $6_q^{H_2O}$  can be described as almost planar quadratic.

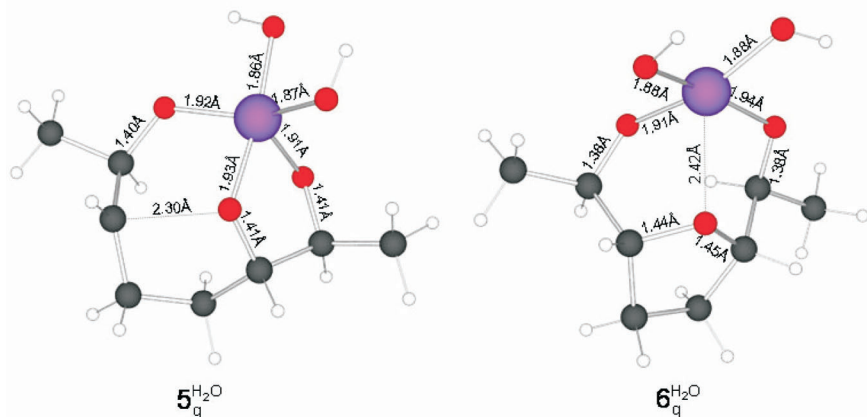


FIG. 4  
Product-forming transition state  $5_q^{H_2O}$  and product  $6_q^{H_2O}$

## CONCLUSIONS

We investigated the permanganate-promoted oxidative cyclization of 1,5-dienes by performing density functional theory calculations (B3LYP/6-311+G\*). We could explain the stereospecificity of this reaction by confirming a mechanism with one permanganate ion adding successively to the two double bonds. A comproportionation between an manganese(V) intermediate and an additional permanganate molecule was found to be unlikely to happen, whereas the addition of a water molecule to this intermediate led to significantly stabilized structures for the second reaction step. Depending on the oxidation state of manganese, different high spin states were shown to be favored. We propose that the reaction proceeds to the manganese(V) ester in the triplet state, followed by the addition of a water molecule and afterwards continuing on the quintet surface to form the product.

## REFERENCES

1. Criegee R.: *Justus Liebigs Ann. Chem.* **1936**, 522, 75.
2. Criegee R.: *Angew. Chem.* **1937**, 50, 153.
3. Criegee R.: *Angew. Chem.* **1938**, 51, 519.
4. Criegee R., Marchand B., Wannowius H.: *Justus Liebigs Ann. Chem.* **1942**, 550, 99.
5. Djerassi C., Engle R. R.: *J. Am. Chem. Soc.* **1953**, 75, 3838.

6. Hofmann K. A.: *Ber. Dtsch. Chem. Ges.* **1912**, 45, 3329.
7. Kondakoff I. L.: *J. Prakt. Chem.* **1899**, 59, 287.
8. Wagner G.: *Ber. Dtsch. Chem. Ges.* **1888**, 21, 3343.
9. Wagner G.: *J. Russ. Phys. Chem. Soc.* **1895**, 27, 219.
10. Lemieux R. U., Von Rudloff E.: *Can. J. Chem.* **1955**, 33, 1710.
11. Frunzke J., Von Rudloff E.: *Can. J. Chem.* **1955**, 33, 1701.
12. Veldkamp A., Frenking G.: *J. Am. Chem. Soc.* **1994**, 116, 4937.
13. Pidun U., Boehme C., Frenking G.: *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2817.
14. DelMonte A. J., Haller J., Houk K. N., Sharpless K. B., Singleton D. A., Strassner T., Thomas A. A.: *J. Am. Chem. Soc.* **1997**, 119, 9907.
15. Dapprich S., Ujaque G., Maseras F., Lledos A., Musaev D. G., Morokuma K.: *J. Am. Chem. Soc.* **1996**, 118, 11660.
16. Torrent M., Deng L., Duran M., Sola M., Ziegler T.: *Organometallics* **1997**, 16, 13.
17. Norrby P.-O., Rasmussen T., Haller J., Strassner T., Houk K. N.: *J. Am. Chem. Soc.* **1999**, 121, 10186.
18. Norrby P.-O., Kolb H. C., Sharpless K. B.: *Organometallics* **1994**, 13, 344.
19. Frunzke J., Loschen C., Frenking G.: *J. Am. Chem. Soc.* **2004**, 126, 3642.
20. Drees M., Strassner T.: *J. Org. Chem.* **2006**, 71, 1755.
21. Houk K. N., Strassner T.: *J. Org. Chem.* **1999**, 64, 800.
22. Strassner T., Busold M.: *J. Org. Chem.* **2001**, 66, 672.
23. Strassner T.: *Adv. Phys. Org. Chem.* **2003**, 38, 131.
24. Strassner T., Busold M.: *J. Phys. Chem.* **2004**, 108, 4455.
25. Strassner T., Drees M.: *J. Mol. Struct. (THEOCHEM)* **2004**, 671, 197.
26. Wiberg K. B., Wang Y.-G., Sklenak S., Deutsch C., Trucks G.: *J. Am. Chem. Soc.* **2006**, 128, 11537.
27. Torrent M., Sola M., Frenking G.: *Chem. Rev.* **2000**, 100, 439.
28. Deubel D. V., Frenking G.: *J. Am. Chem. Soc.* **1999**, 121, 2021.
29. Deubel D. V., Frenking G.: *Acc. Chem. Res.* **2003**, 36, 645.
30. Strassner T.: *Catalysis by Metal Complexes*, Vol. 25, pp. 253–268. Springer Verlag, Berlin, Heidelberg, New York 2002.
31. Klein E., Rojahn W.: *Tetrahedron* **1965**, 21, 2353.
32. Boeseken J.: *Rec. Trav. Chim. Pays-Bas* **1926**, 45, 838.
33. Carlsen P. H. J., Katsuki T., Martin V. S., Sharpless K. B.: *J. Org. Chem.* **1981**, 46, 3936.
34. De Champdore M., Lasalvia M., Piccialli V.: *Tetrahedron Lett.* **1998**, 39, 9781.
35. Donohoe T. J., Butterworth S.: *Angew. Chem., Int. Ed.* **2003**, 42, 948.
36. Donohoe T. J., Winter J. J. G., Helliwell M., Stemp G.: *Tetrahedron Lett.* **2001**, 42, 971.
37. Piccialli V., Caserta T.: *Tetrahedron Lett.* **2004**, 45, 303.
38. Piccialli V., Cavallo N.: *Tetrahedron Lett.* **2001**, 42, 4695.
39. Sinha S. C., Keinan E., Sinha S. C.: *J. Am. Chem. Soc.* **1998**, 120, 9076.
40. Sinha S. C., Keinan E.: *Pure Appl. Chem.* **2002**, 74, 93.
41. D'Souza L. J., Sinha S. C., Lu S. F., Keinan E., Sinha S. C.: *Tetrahedron* **2001**, 57, 5255.
42. Baldwin J. E., Crossley M. J., Lehtonen E. M. M.: *Chem. Commun.* **1979**, 918.
43. Fernandez J. J., Souto M. L., Norte M.: *Nat. Prod. Rep.* **2000**, 17, 235.
44. Alali F. Q., Liu X.-X., McLaughlin J. L.: *J. Nat. Prod.* **1999**, 62, 504.
45. Wagner H., Harms K., Koert U., Meder S., Boheim G.: *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 2643.
46. Dutton C. J., Banks B. J., Cooper C. B.: *Nat. Prod. Rep.* **1995**, 12, 165.

47. Koert U.: *Synthesis* **1995**, 115.
48. Kocienski P. J., Brown R. C. D., Pommier A., Procter M., Schmidt B.: *J. Chem. Soc., Perkin Trans. 1* **1998**, 9.
49. Walba D. M., Przybyla C. A., Walker C. B., Jr.: *J. Am. Chem. Soc.* **1990**, 112, 5624.
50. Brown R. C. D., Keily J. F.: *Angew. Chem., Int. Ed.* **2001**, 40, 4496.
51. Sable H. Z., Powell K. A., Katchian H., Niewoehner C. B., Kadlec S. B.: *Tetrahedron* **1970**, 26, 1509.
52. Wolfe S., Ingold C. F.: *J. Am. Chem. Soc.* **1981**, 103, 940.
53. Pode J. S. F., Waters W. A.: *J. Chem. Soc.* **1956**, 717.
54. Kirschenbaum L. J., Meyerstein D.: *Inorg. Chim. Acta* **1981**, 53, L99.
55. Walba D. M., Wand M. D., Wilkes M. C.: *J. Am. Chem. Soc.* **1979**, 101, 4396.
56. Schroeder D., Shaik S., Schwarz H.: *Acc. Chem. Res.* **2000**, 33, 139.
57. Frisch M. J. T. G. W., Schlegel H. B., Scuseria G. E., Robb M. A., Cheeseman J. R., Montgomery J. A., Jr., Vreven T., Kudin K. N., Burant J. C., Millam J. M., Iyengar S. S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G. A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J. E., Hratchian H. P., Cross J. B., Bakken V., Adamo C., Jaramillo J., Gomperts R., Stratmann R. E., Yazyev O., Austin A. J., Cammi R., Pomelli C., Ochterski J. W., Ayala P. Y., Morokuma K., Voth G. A., Salvador P., Dannenberg J. J., Zakrzewski V. G., Dapprich S., Daniels A. D., Strain M. C., Farkas O., Malick D. K., Rabuck A. D., Raghavachari K., Foresman J. B., Ortiz J. V., Cui Q., Baboul A. G., Clifford S., Cioslowski J., Stefanov B. B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R. L., Fox D. J., Keith T., Al-Laham M. A., Peng C. Y., Nanayakkara A., Challacombe M., Gill P. M. W., Johnson B., Chen W., Wong M. W., Gonzalez C., Pople J. A.: *Gaussian 03*, Revision C.02. Gaussian, Inc., Wallingford (CT) 2004.
58. Becke A. D.: *J. Chem. Phys.* **1993**, 98, 5648.
59. Lee C. Y. W., Parr R. G.: *Phys. Rev. B* **1988**, 37, 785.
60. Stephens P. J. D. F. J., Chabalowski C. F., Frisch M. J.: *J. Phys. Chem.* **1994**, 98, 11623.
61. Vosko S. H., Wilk L., Nusair M.: *Can. J. Phys.* **1980**, 58, 1200.
62. Binning R. C., Jr., Curtiss L. A.: *J. Comput. Chem.* **1990**, 11, 1206.
63. Clark T., Chandrasekhar J., Spitznagel G. W., Schleyer P. v. R.: *J. Comput. Chem.* **1983**, 4, 294.
64. Hay P. J.: *J. Chem. Phys.* **1977**, 66, 4377.
65. Krishnan R., Binkley J. S., Seeger R., Pople J. A.: *J. Chem. Phys.* **1980**, 72, 650.
66. McGrath M. P., Radom L.: *J. Chem. Phys.* **1991**, 94, 511.
67. Raghavachari K., Trucks G. W.: *J. Chem. Phys.* **1989**, 91, 2457.
68. Wachters A. J. H.: *J. Chem. Phys.* **1970**, 52, 1033.
69. Frisch M. J., Pople J. A., Binkley J. S.: *J. Chem. Phys.* **1984**, 80, 3265.
70. Reiher M., Salomon O., Hess B. A.: *Theor. Chem. Acc.* **2001**, 107, 48.
71. Salomon O., Reiher M., Hess B. A.: *J. Chem. Phys.* **2002**, 117, 4729.
72. Schlegel H. B.: *J. Comput. Chem.* **1982**, 3, 214.
73. Schaftenaar G., Noordik J. H.: *J. Comput.-Aided Mol. Des.* **2000**, 14, 123.