

Predictions of Geometries and Multiplicities of the Manganese–Oxo Intermediates in the Jacobsen Epoxidation

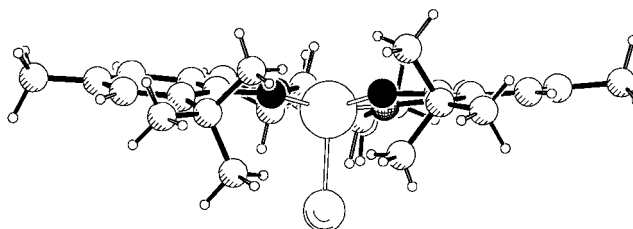
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ABSTRACT



The geometries and multiplicities of models of the manganese(III)–salen catalyst and the manganese(V)–oxo intermediate in the Jacobsen epoxidation were explored with density functional theory (Becke3LYP). Mn(III) complexes are quintet ground states, while ligands influence whether quintet, triplet, or singlet states are lowest in energy for Mn(V)–oxo complexes. Geometries and multiplicities and their implications for stereoselectivity are described.

Jacobsen's manganese–salen catalysts such as **1** (Figure 1) promote the stereoselective conversion of prochiral olefins to chiral epoxides with enantiomeric excesses regularly better than 90%¹ and sometimes exceeding 98%.² The origin of the selectivity has not been explained definitively, although several mechanisms have been proposed.³

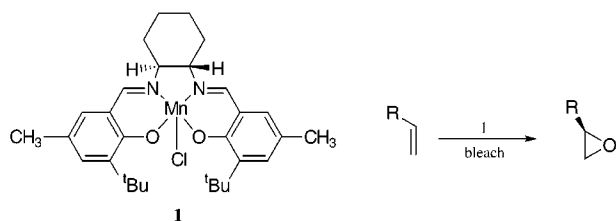


Figure 1. Jacobsen catalyst for the asymmetric epoxidation of alkenes.

The oxygen transfer is a two-step catalytic cycle: oxygen is transferred from an oxidant to the manganese(III) catalyst; subsequently, the activated oxygen is delivered to the alkene.^{4,5} Both concerted and stepwise pathways have been

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proposed for the epoxidation of alkenes.^{3g} The multiplicity of the intermediate should influence whether the concerted or stepwise reaction can occur, although spin-orbit coupling will accelerate intersystem crossing during reactions involving multiplicity changes. Groves has recently demonstrated experimentally the influence of multiplicity in epoxidations by manganese(V)-oxo porphyrins.⁶

The high enantioselectivity of this reaction is surprising, and its origin remains elusive. Three questions stand out: (1) How can the relatively flat catalyst⁷ give such impressive selectivity? (2) What is the trajectory of approach of alkenes (top, side, or bottom on **1**) to the MnO intermediate? (3) What is the timing of bond formation between the alkene and transferred oxygen?

We explored these issues in more detail by computing the geometries of the manganese-oxo intermediates as a prelude to transition state searches. Because of the size of the system, we chose to study model systems **2–5** (see Figure 2).

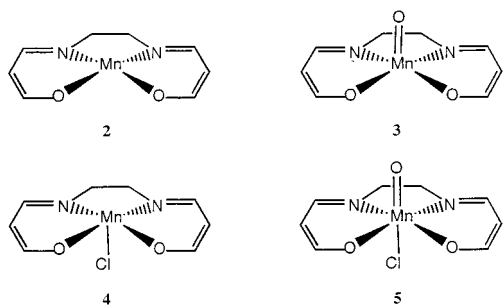


Figure 2. Model systems, **2–5**, employed in calculations.

Density functional theory calculations with the B3LYP hybrid functional were performed using GAUSSIAN-94.^{8–10} The split valence double- ζ (DZ) basis set 3-21G and double- ζ (DZ) plus polarization basis set 6-31G* have been employed in the DFT calculations together with DZ¹¹ and triple- ζ (TZ)¹² valence basis sets for manganese. Results for all three basis sets are given in the Supporting Information. The 6-31G*/TZ results are discussed here.

Manganese has a 3d⁷ electronic configuration, and its oxidation states span the whole range between II and VII.¹³ Mn(III) favors an octahedral coordination sphere, while little is known about manganese(V) compounds. Manganese(III) compounds have d⁴ electronic configurations. In an octahedral ligand field, the three degenerate t_{2g} orbitals are lower

in energy than the two e_g orbitals; both the low-spin singlet and intermediate spin triplet (t_{2g}⁴) configurations, or—in a weak field—the high-spin (t_{2g}³e_g) quintet configuration, are accessible. Model system **4** with five substituents should have either a square-pyramidal or a trigonal-bipyramidal geometry.

The manganese(V)-oxo intermediate is formally d², which should lead to a triplet ground state. A strong asymmetric field can split the degeneracy of occupied orbitals, leading to a singlet ground state. Alternatively, the oxo ligand, rather than acting as O²⁻, can donate two electrons to manganese, producing an O⁰ Mn(III) d⁴ configuration, and a quintet multiplicity.

For all model systems, singlet, triplet, and quintet multiplicities have been computed. For related manganese systems, density functional calculations give reasonable energetic ordering of states of different multiplicities.¹⁴ Table 1 gives

Table 1. Becke3LYP/6-31G* (CHCINO)/TZ (Mn) Relative Energies (kcal/mol) for **2–5**

	2: Mn(III)			4: Mn(III)Cl			3: Mn(V)O			5: Mn(V)O/Cl		
	s	t	q	s	t	q	s	t	q	s	t	q
ΔE	45.7	27.1	0.0	40.2	19.5	0.0	0.0	3.5	11.2	10.2	0.0	2.0
S^2		2.6	6.1		2.1	6.1		2.1	6.1		2.9	6.1

the energies of the optimized catalysts: **2** (a free cation), **4** (**2** plus a chloride ligand), and the manganese-oxo species **3** (free cation) and **5** (**3** plus a chloride ligand). In the Table, s, t, and q refer to singlet, triplet and quintet multiplicities. The $\langle S^2 \rangle$ values measure whether the spin state is pure singlet, triplet or quintet ($S^2 = 0, 2, \text{ and } 6$, respectively).

The structures of the triplets and quintets of the Mn(III) species, **2** and **4**, are shown in Figure 3; the singlets are very high in energy and are puckered into a tetrahedral conformation. These are not shown.

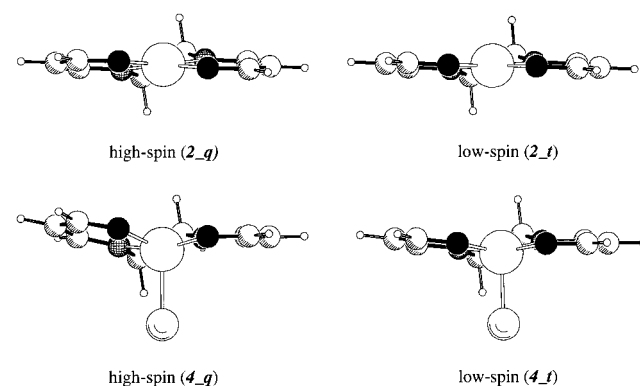


Figure 3. Quintet and triplet state geometries of the manganese(III) model systems.

To compare the calculations with experimental data, a structure-based search for the central fragment **2** in the

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Cambridge crystallographic database was performed; this resulted in location of 46 structures.¹⁵ The calculations on models **2** and **4** are in reasonably good agreement with these experimental values. A recent study of manganese–oxo dimer complexes gives similar results.¹⁴ The relevant data are summarized in the Supporting Information.

The two Mn(III) model systems have very large preferences for high-spin quintet states (Table 1). The ligand field does not split the degeneracy of the d orbitals significantly—the tendency to avoid spin-pairing dominates. The Mn(III) catalysts are predicted to be high spin (quintets).

For the manganese(V)–oxo systems, a different pattern emerges. The free cation, **3**, is predicted to have nearly degenerate singlet and triplet states, with the singlet lower by 4 kcal/mol.

Upon coordination of chloride to form **5**, the situation changes: now the triplet and quintet states are nearly degenerate; the quintet state is predicted to be only 1–2 kcal/mol higher than the triplet. The influence of the sixth ligand is to reduce the energy difference between the e and t sets of partially occupied d orbitals. A low-spin (singlet or triplet) complex is favored with weak coordination or absence of a sixth ligand, while a higher spin (quintet or triplet) state occurs upon association of a stronger ligand. The rates of Mn–oxo reactions could be influenced by spin-state crossing effects as in other Mn–oxo⁶ or Fe–oxo systems.^{16,17}

This implies that different experimental results may occur with different ligands, since they will influence spin multiplicities, and potentially the relative rates of stereospecific concerted and stepwise nonconcerted processes. Experimentally, weak ligands, like pyridine *N*-oxide, increase the enantioselectivity.¹⁸ The nature of the ligand might play a role for the stereoselectivity of the reaction, since the reaction of a high-spin oxo intermediate could lead directly to high-spin product in a concerted fashion with conservation of spin, while a low-spin species would have to undergo a change of spin multiplicity during reaction, which could give stepwise processes a chance to compete with concerted.

The three-dimensional geometries of the Mn(V)–oxo complexes calculated by the manganese triple- ζ basis with a B3LYP/6-31G* basis set are shown in Figure 4. The approach from the backside is hindered in a similar way for all the structures, while the pentacoordinated singlet **3_s** does have a larger twist angle and could increase the stereoselectivity for trans alkenes. The flatter structures, **3_t** and **3_q**,

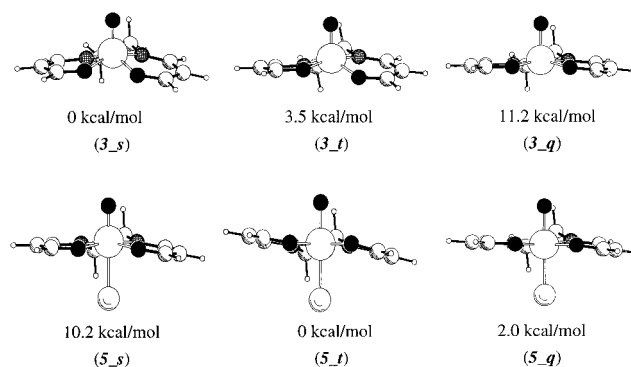


Figure 4. Manganese(V) model compounds calculated by the manganese triple- ζ basis/Becke3LYP/6-31G*.

do not discriminate between the two sides and are not expected to induce the same stereoselectivity. All hexacoordinated structures do not show a large twist angle. The actual catalyst with its *tert*-butyl groups (Figure 1) will discriminate between different pathways with the triplet structure **5_t**.

Conclusions

The Mn(III) systems are high-spin ground states. Density functional theory calculations with a triple- ζ basis for manganese and a 6-31G* basis set for all other atoms provide geometries which are in very good agreement with experimental X-ray structures. The calculations indicate that the active intermediate Mn–oxo species in the Jacobsen epoxidation may be either a high-spin quintet or triplet, depending upon the nature of the ligands.

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Note Added in Proof: A related investigation, including transition states, has just been published: Linde, C.; Åkermark, B.; Norrby, P.-O.; Svensson, M. *J. Am. Chem. Soc.* **1999**, *121*, 3083.

Supporting Information Available: Tables of bond lengths for Mn crystal structures, of comparisons to calculations on model systems, and of total and relative energies for **2–5** with three basis sets and a list of the Cambridge reference codes used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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