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The Mechanism of Permanganate Oxidation of Sulfides and Sulfoxides

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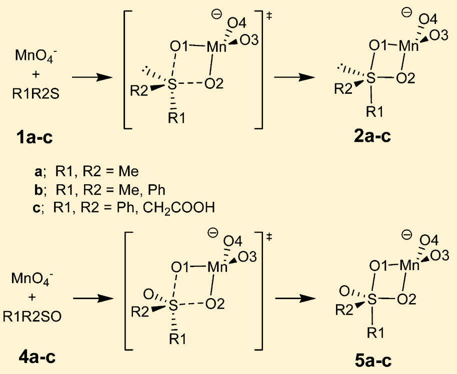
S Supporting Information

ABSTRACT: Coupled-cluster (CCSD) and density functional computations are used to investigate historically competing mechanisms for the permanganate oxidation of sulfides and sulfoxides. The calculations all lead to a mechanism of 1,3-dipolar cycloaddition of permanganate, as opposed to historical mechanisms of attack of the sulfur atom by one O or by Mn. Such a mechanism, reminiscent of ozonolysis, may prevail in most permanganate oxidations. The ab initio activation enthalpies are in reasonable agreement with the experimental data; the ab initio activation entropies are not, possibly because of problems with Eyring equation assumptions.



INTRODUCTION

Permanganates are well-known for oxidations in organic chemistry,[1] including oxidations of organic sulfides and sulfoxides.[2] However, their mechanisms are not as well-defined because of the complexities in the aqueous chemistry of manganese oxyanions. Computational studies now generally agree that the oxidation of alkenes by permanganate[3−6] and other MO_4^{n-} oxidants[6,7] involve a cyclic Mn(V) intermediate (Figure 1).[3] However, in two recent reviews there is continuing speculation that the intermediate is preceded by a 5-coordinate organometallic complex, and in addition, the rapid steps from the cyclic intermediate into product are not fully understood.[8,9] As Ess has noted,[6] the cyclic intermediate is reminiscent of the 1,2,3-trioxolane intermediate in ozonolysis,[10] and substituent effects upon the reaction kinetics are similar.[11] We suggest fully adopting the term 1,3-dipolar cycloaddition in both the ozone and MO_4^{n-} cases.

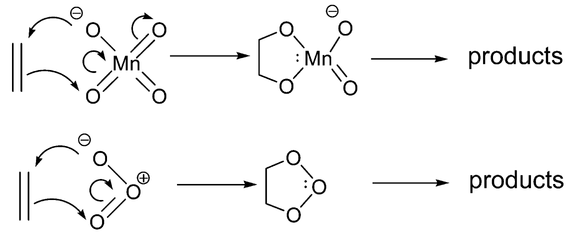


Figure 1. Alkene oxidations involving initial 1,3-dipolar cycloadditions.

A similar intermediate for the permanganate oxidation of organic sulfides was proposed but immediately discarded by Banerji[12] (and similarly by Ruff for periodate oxidation[13]). Instead, proposals of (i) single-electron transfer, (ii) direct O-atom transfer, and (iii) initial Mn−S interaction have been considered, with versions of the latter being favored in recent reviews (Figure 2).[8,9]

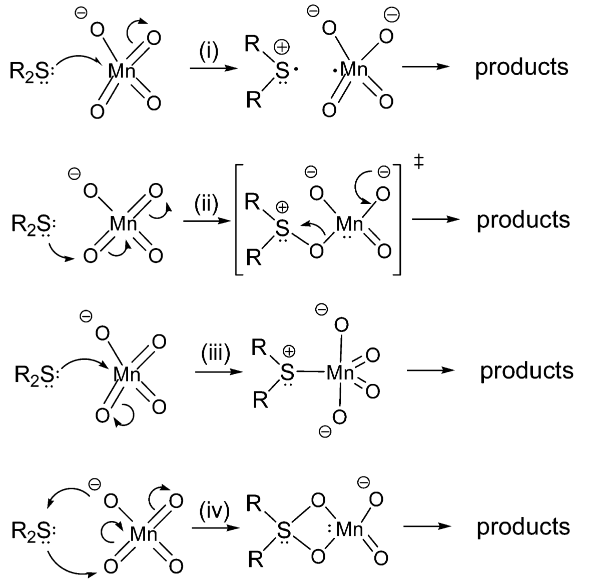


Figure 2. Four hypothetical mechanisms for sulfide oxidation found in the literature. Mechanism iv, the least popular one to date, is the one found to be correct from our work.

To ascertain the mechanism of the permanganate oxidation of organic sulfides we have performed density-functional-theory

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(DFT) geometry optimizations and coupled-cluster (CCSD) single-point energy computations of mechanisms ii–iv, accepting the strong evidence that mechanism i does not occur. The calculations were performed for dimethylsulfide (**1a**), thioanisole (**1b**), and phenylthioacetic acid (**1c**); the latter is of interest because activation energies and entropies have been determined experimentally for it.[14,15] The studied compounds at various reaction stages are labeled as per Table 1; prime notation indicates van der Waals complexes.

Table 1. Compound Notation[a]

label	entity
1	R1R2S + MnO_4^-
1′	R1R2S·MnO_4^-
2	R1R2SO_4Mn^-
3′	R1R2SO·MnO_3^-
3	R1R2SO + MnO_3^-
4	R1R2SO + MnO_4^-
4′	R1R2SO·MnO_4^-
5	R1R2SO_5Mn^-
6′	R1R2SO_2·MnO_3^-
6	R1R2SO_2 + MnO_3^-

[a] **1a**: R1 = R2 = Me. **1b**: R1, R2 = Ph, Me. **1c**: R1, R2 = Ph, CH_2COOH.

■ COMPUTATIONAL DETAILS

Geometry optimizations and vibrational frequency calculations were performed at the B3LYP[16]/B1 level of theory with Gaussian03 (E.01) software.[17] B1 refers to a mixed basis set of LANL2DZ for the Mn atom and 6-31G(d) for other atoms (C, H, O, and S), with spherical-harmonic sets of *d* functions. Transition state structures were located using opt = (ts, noeigentest, calcfc) algorithms,[18,19] and each optimized transition state structure was subjected to a vibrational frequency analysis to confirm that the structure had one imaginary frequency only and that the magnitudes of all frequencies should be greater than the residual noise of the rotational and translational "frequencies". Furthermore, each transition state was confirmed to be on the desired reaction path by "plus-and-minus-displacement" minimization runs: the transition state was displaced ~0.05 Å or 5° along the imaginary frequency normal mode in both directions, and the two displaced structures were optimized to the nearest minima structures. The B3LYP vibrational frequencies were scaled[20] (keyword SCALE = 0.9806) for use in computing entropies and thermodynamic energy corrections, for which Gaussian codes use standard rigid-rotor/harmonic oscillator (RRHO) statistical thermodynamic formulas.

Single-point energies were computed at B3LYP/B1 geometries using an added polarizable continuum model (SCRF = PCM) for an aqueous solvent effect,[21] using Gaussian09 (B.01).[22] Levels of theory tested were B3LYP, perturbation theory (MP2, MP3),[23] and the coupled-cluster approximation (CCSD).[24] Gaussian09 was also used for partial charge computation (pop = npa).[25]

Finally, MOLPRO2008[26] was used to compute CCSD single-point energies with larger basis sets (but no PCM) to derive extended basis set corrections to append to the CCSD/B1/PCM//B3LYP/B1 energies for improved accuracy. Preliminary tests on Δ*E* for **1a′** → [**TS1–2**]**a** revealed that aug-cc-pVDZ produced results within ±7 kJ mol^{-1} of other larger basis sets, which was fortunate because CCSD/aug-cc-pVDZ calculations on our largest molecule (**5c**) needed 503 basis functions and C_1 symmetry, which challenged our computer. Our final composite method for energies began with CCSD/B1/PCM//B3LYP/B1, added basis set corrections E(CCSD/aug-cc-pVDZ) − E(CCSD/B1), and added thermodynamic corrections from scaled B3LYP/B1.

■ RESULTS AND DISCUSSION

Evidence against Mechanisms ii and iii. Mechanism iii arose from a 1977 suggestion by Sharpless[27] that organometallic complexes, with a direct metal–substrate interaction, be considered for oxidations by oxometal compounds in organic synthesis. However, Ziegler[28] used DFT calculations to point out that addition of C=C to M=O (oxidant MoO_2Cl_2 is unlikely because of the low nucleophilicity of the lone pairs on O, and ensuing DFT work by Strassner and coworkers[3,4,7] have shown that, for MO_4^{n-} + alkenes, the 1,3-dipolar cycloaddition (then called [3 + 2] addition) is a lower-energy pathway than the metal-interacting path (then called [2 + 2] addition) by a remarkable 170 kJ mol^{-1} at that level of theory. It remains to be seen if a metal interaction is more relevant with R_2S instead of with C=C. Our best attempt at locating an organometallic intermediate (Figure 3a) shows that such a complex would be 740 kJ mol^{-1} (B3LYP) uphill from

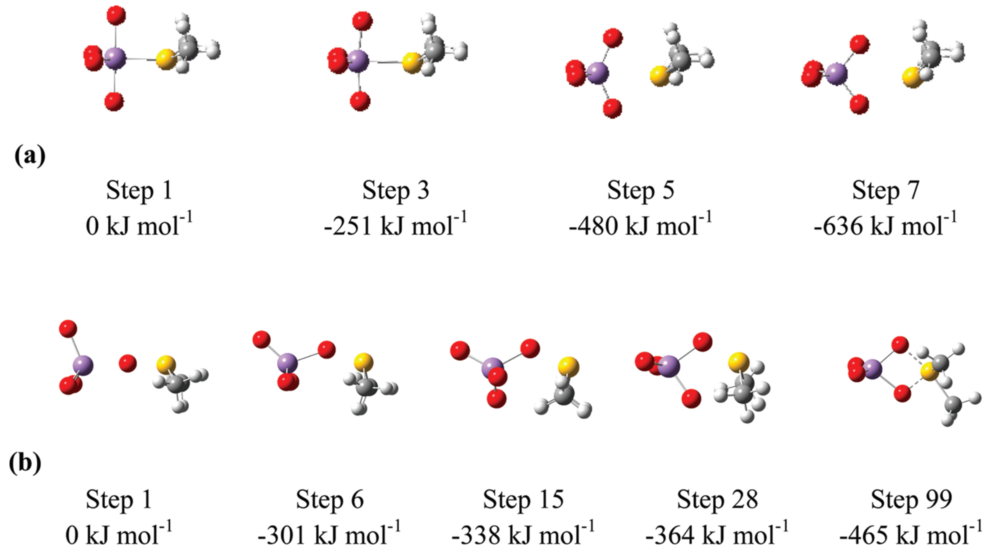

Figure 3. Snapshots of attempted B3LYP/B1 optimizations of (a) a mechanism iii intermediate and (b) a mechanism ii transition state, demonstrating their nonexistence.

the reactants; the geometry optimization rapidly dissociated the supposed complex. Thus, as for alkene oxidations, we conclude that a Sharpless-type intermediate cannot exist with oxidants of the type MO_4^{n-}.

Mechanism ii was suggested by Banerji[12] on the basis of analogy with a proposal by Ruff[13] for periodate oxidation of sulfides. He had drawn the transition state with a linear geometry at the transferring O atom, suggesting in his text that it operates as an S_N2-type reaction. Two attempts at locating such a transition state show a continuous migration toward, and convergence upon, the 1,3-dipolar-cycloaddition transition state (Figure 3b), whereas a third attempt resulted in an internal rotation transition state of a reactant complex of sulfide with permanganate. Thus, we conclude that the S_N2-style mechanism ii must also be incorrect.

Formation of the Cycloaddition Intermediate. The 1,3-dipolar cycloaddition (mechanism iv) was observed on the B3LYP potential energy surfaces (PES) for oxidation of all three sulfides **1a−c** and all three sulfoxides **4a−c**. The transition states **TS1−2** and **TS4−5** have electron-pair geometries about the S atom that are intermediate between square pyramid and trigonal bipyramid and lead to trigonal bipyramid cyclic intermediates **2a−c** and **5a−c** (Figure 4).

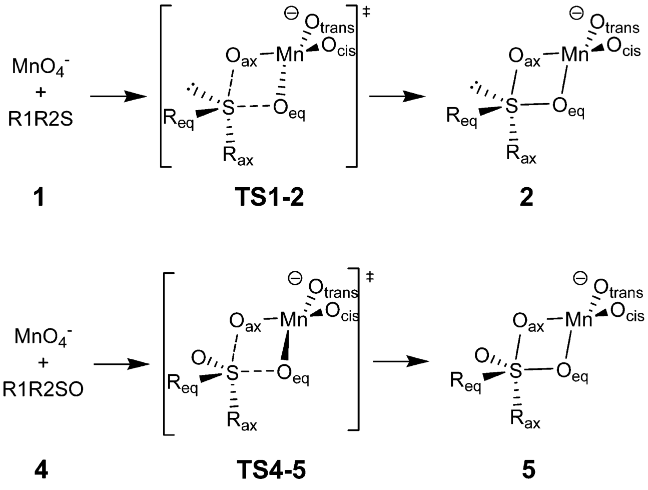

Figure 4. B3LYP results for sulfide/sulfoxide oxidation: a 1,3-dipolar cycloaddition.

The trigonal bipyramid structure makes the two alkyl positions inequivalent in the intermediate (R_{ax} and R_{eq}), giving rise to isomers when R1 and R2 are different groups (**2b**,**c** and **5b**,**c**). For the thioanisole intermediate (**2b**), the Ph-axial isomer is the important one, being 6 kJ mol^{-1} lower in energy (B3LYP/B1) than the Me-axial isomer, and being the one that directly follows the transition state **TS1b2b**. For **5b**, the same situation exists, but the isomer energy difference is 1 kJ mol^{-1}. For the phenylthioacetic acid intermediate (**2c**), there are additional isomer possibilities arising from intramolecular hydrogen bonding: depending on whether the H bond is directed to O_{ax}, O_{eq}, O_{cis}, or the lone pair on S, the relative energies are 0, 2, 10, and 33 kJ mol^{-1}, respectively. The lowest-energy form (the first of these four) has an equatorial phenyl group. For **5c**, depending on whether the H bond is directed to O_{ax}, O_{eq}, O_{cis}, or the sulfoxide oxygen, the relative energies are 9, 8, 16, and 0 kJ mol^{-1}, respectively; the lowest-energy form (the fourth of these four) has an axial phenyl group.

The two bridging oxygen atoms are also inequivalent; in the intermediates, the sulfur is slightly more strongly bound to its equatorial oxygen (O_{eq}) than its axial one (O_{ax}). The optimized bond lengths to O_{ax} and O_{eq} appear in Table 2 for the lowest-energy isomer of each species.

Table 2. B3LYP Optimized Bond Lengths (Å)

	TS1a2a	TS1b2b	TS1c2c	TS4a5a	TS4b5b	TS4c5c
R(Mn−O_{eq})	1.682	1.690	1.691	1.669	1.674	1.676
R(Mn−O_{ax})	1.682	1.690	1.712	1.668	1.676	1.666
R(S−O_{eq})	2.098	2.072	2.020	2.139	2.124	2.118
R(S−O_{ax})	2.098	2.045	2.133	2.116	2.056	2.085
	2a	**2b**	**2c**	**5a**	**5b**	**5c**
R(Mn−O_{eq})	1.826	1.832	1.823	1.830	1.835	1.837
R(Mn−O_{ax})	1.757	1.763	1.782	1.769	1.772	1.781
R(S−O_{eq})	1.679	1.669	1.678	1.655	1.647	1.644
R(S−O_{ax})	1.890	1.860	1.972	1.781	1.773	1.740

The experimental values for the activation enthalpies $\Delta^{\ddagger}H_{298}(\mathbf{1c'}{-}\mathbf{2c})$ and $\Delta^{\ddagger}H_{298}(\mathbf{4c'}{-}\mathbf{5c})$ are 18 and 20 kJ mol^{-1}, respectively.[14,15] Table 3 shows the predictions for the 1,3-dipolar addition mechanism at various levels of theory. Wiberg and co-workers[5] have already noted some very poor energy predictions by Møller−Plesset perturbation theory (MP2) for permanganate reaction. The reason for this failure is that perturbation theory requires a good zeroth order description of the electronic state by a single-configuration Hartree−Fock wave function. Hartree−Fock energies are clearly not a good zeroth-order description of permanganate oxidations as evidenced in Table 3. The true activation enthalpy values lie between the CCSD and B3LYP predictions, constituting a satisfying check on the mechanism.

Table 3. Activation Enthalpies (kJ mol^{-1})[a]

	$\Delta^{\ddagger}H_{298}(\mathbf{1c'}{-}\mathbf{2c})$	$\Delta^{\ddagger}H_{298}(\mathbf{4c'}{-}\mathbf{5c})$
basis correction[b]	−17	−4
thermal correction[c]	−6	−3
HF	−212	−133
MP2	378	369
MP3	−359	−302
CCSD	−3	9
B3LYP gas	55	41
B3LYP	30	29
expt	**18**[d]	**20**[e]

[a] All calculations employed B3LYP/B1 gas-phase geometries, the B1 basis set, the Gaussian09 PCM solvent effect (except "B3LYP gas"), and include the basis and thermal corrections listed. [b] Calculated as ΔE(CCSD/aug-cc-pVDZ) − ΔE(CCSD/B1) with MOLPRO2008. [c] Calculated from scaled B3LYP/B1 frequencies. [d] Ref 14. [e] Ref 15.

Table 4 summarizes the computed energies of these six cycloadditions, considering only the path to the lowest-energy isomer in each case. For sulfoxides **4a** and **4b**, the cycloaddition is predicted to be faster and significantly more exothermic than for the corresponding sulfides **1a** and **1b**. Phenylthioacetic acid (**1c**) is predicted to react faster than **1a** or **1b** for reasons not clear to us; there is a hydrogen bond from the phenylthioacetic

Table 4. Calculated Energies (kJ mol^{-1}) of the 1,3-Dipolar Cycloadditions[a]

compound	$\Delta^{\ddagger}E_{\mathrm{elec}}$	$\Delta^{\ddagger}H_{298}$	ΔE_{elec}	ΔH_{298}
1a′ → **2a**	19	13	−21	−24
1b′ → **2b**	23	18	−17	−19
1c′ → **2c**	3	−3	−31	−34
4a′ → **5a**	10	7	−67	−65
4b′ → **5b**	11	8	−61	−60
4c′ → **5c**	8	5	−70	−67

[a] CCSD/B1/PCM//B3LYP/B1 results with basis corrections added.

acid to the incoming permanganate, which perhaps assists the reaction.

Experimentally determined Eyring-plot activation entropies ($\Delta^{\ddagger}S$) for **1c** → **2c**[14] and **4c** → **5c**[15] are −176 and −160 J mol^{-1} K^{-1}, respectively. Use of these values to test the 1,3-dipolar cycloaddition mechanism was difficult, as these entropies are challenging to predict ab initio. Since this reaction involves two compounds becoming one intermediate in aqueous solution, the gas-phase assumptions of computational chemistry codes cause large errors in entropy. We estimate that the gas-phase entropy loss due to association is about 100 ± 40 J mol^{-1} K^{-1} more negative than in the condensed phase. Our crude value arises by assuming that the translational entropy of a typical molecule drops from 170 to 85 J mol^{-1} K^{-1} (from three particle-in-a-box modes with mass 120 amu to three harmonic oscillators with phonon frequency 20 cm^{-1}), and the rotational entropy of a typical molecule drops from 105 to 90 J mol^{-1} K^{-1} (from three rigid-rotor modes with $mr^2 = 390$ amu Å^2 to one such mode plus two harmonic oscillators with phonon frequency 20 cm^{-1}).[29] As it turns out, adding this correction to computed gas-phase RRHO values happens to give similar results to alternative gas-phase RRHO results in which a van-der-Waals or H-bonded complex of the two reactants together (a "supermolecule" calculation) is considered, instead of separate reactant calculations. This fortuitous occurrence is because the van-der-Waals-supermolecule RRHO calculation underpredicts the translational and rotational entropies of the individual reactants but *overpredicts* the vibrational entropies because of the use of harmonic oscillator estimates for loose internal rotation modes. (Note that neither the gas-phase approximation nor the use of harmonic oscillator formulas for internal rotations has much adverse effect on energies and enthalpies.)

Table 5 shows the computed entropies of these six reactions, computed three different ways. Given the discussion above, we estimate the entropies of reaction (ΔS) and activation ($\Delta^{\ddagger}S$) to be −70 ± 40 and −65 ± 40 J mol^{-1} K^{-1}, respectively. The Eyring-plot $\Delta^{\ddagger}S$ values of −176 and −160 lie outside the [−25, −105] range predicted here. This disagreement could be rectified if the Eyring equation were missing a factor of 0.0003 (because of neglect of activity and transmission coefficients,[30] for instance), although such a factor seems quite extreme. We are eager to know if there is a known successful match of Eyring plot and ab initio entropies of activation in the literature for *any* bimolecular reaction, as we have not come across any.

Table 5. Entropies (J mol^{-1} K^{-1}) of the 1,3-Dipolar Cycloadditions, from B3LYP Calculations

compound	$\Delta^{\ddagger}S_{298}$[a]	$\Delta^{\ddagger}S_{298}$[b]	$\Delta^{\ddagger}S_{298}$[c]	ΔS_{298}[a]	ΔS_{298}[b]	ΔS_{298}[c]
1a → **2a**	−158	−56	−58	−164	−62	−64
1b → **2b**	−170	−78	−70	−167	−75	−67
1c → **2c**	−171	−56	−71	−166	−51	−66
4a → **5a**	−162	−62	−62	−173	−73	−73
4b → **5b**	−165	−55	−65	−170	−60	−70
4c → **5c**	−173	−65	−73	−176	−68	−76

[a] Reactants computed separately. [b] Reactants computed as a supermolecule. [c] Reactants computed separately but +100 J mol^{-1} K^{-1} correction added for condensed-phase effects (see text).

Finally, we note that the Eyring plot analyses of Lee and Chen[14,15] suggest that the faster rate of oxidation of the sulfoxide **4c** versus the sulfide **1c** (a factor of 3) is an entropic, rather than enthalpic, effect. Our data is not accurate enough to confirm this.

Partial Charges. A past argument for erroneous mechanism iii had been that two apparent nucleophiles (e.g., O and C=C, or in our case, O and S) are unlikely to make the initial interaction.[8] However, 1,3-dipolar cycloadditions allow for the provision of one electrophilic O atom as well as a nucleophilic one. Computed B3LYP/B1 partial charges are shown in Table 6.

Table 6. B3LYP/B1 NPA Partial Charges for the Oxidation of Me_2S (1a) and Me_2SO (4a) with Permanganate Ion

compound	S	Mn	O_{ax}	O_{eq}
1a′ (vdW complex)	0.15	0.38	−0.34	−0.34
TS1a2a	0.74	0.40	−0.54	−0.54
2a	1.21	0.47	−0.75	−0.75
4a′ (vdW complex)	1.24	0.38	−0.35	−0.35
TS4a5a	1.60	0.41	−0.52	−0.52
5a	2.11	0.51	−0.74	−0.77

As the sulfur atom is oxidized in this cycloaddition (partial charge increases of 1.06e and 0.87e for oxidation of **1a** and **4a** respectively), it is the oxygen atoms (not Mn) that act as electrophiles in accepting this excess electron density.

Suppose, rather than considering MnO_4^- as an ionic complex of Mn^{7+} and O^{2-} ions (acceding to formal oxidation states), one considers it as an ionic complex of $Mn^{+1/3}$ and $O^{-1/3}$ ions (acceding to Table 6 partial charges). One might then describe the role of Mn as a *template* and the $O^{-1/3}$ ions as the true oxidizing agents in this ion. When viewed in this way, the O-atom electrophilicity should be considered appreciable enough to make a facile 1,3-dipolar attack understandable. Furthermore, given Strassner's observations with MO_4^{n-} + alkene calculations,[3,4,7] it would be logical to speculate that *most organic oxidations by oxyanions, including permanganate, periodate, and perruthenate, likely occur via initial 1,3-dipolar cycloaddition.*

Fate of the Intermediate. In neutral pH conditions, the final products are sulfoxides, sulfones, and Mn in the Mn(IV) oxidation state (brown precipitate MnO_2).[8,9] There are a few possibilities (Figure 5) for the ensuing step after the 1,3-dipolar cycloaddition, just as there are in the case of permanganate oxidation of alkenes: (i) metathesis dissociation, (ii) hydrolysis, (iii) disproportionation with another Mn(V) complex, or (iv) comproportionation with another Mn(VII) permanganate ion.

It will take some time to explore these possibilities computationally, but for now we examined the metathesis dissociation possibility. For all six intermediates **2a**–**c** and **5a**–**c**, transition states for this second step were found. Each case has a choice of two possible ways to distribute the two bridging O atoms among the products; in tests for **2a** → **3a**, the lower-energy path was cleavage of the Mn–O_{eq} and S–O_{ax} bonds, as

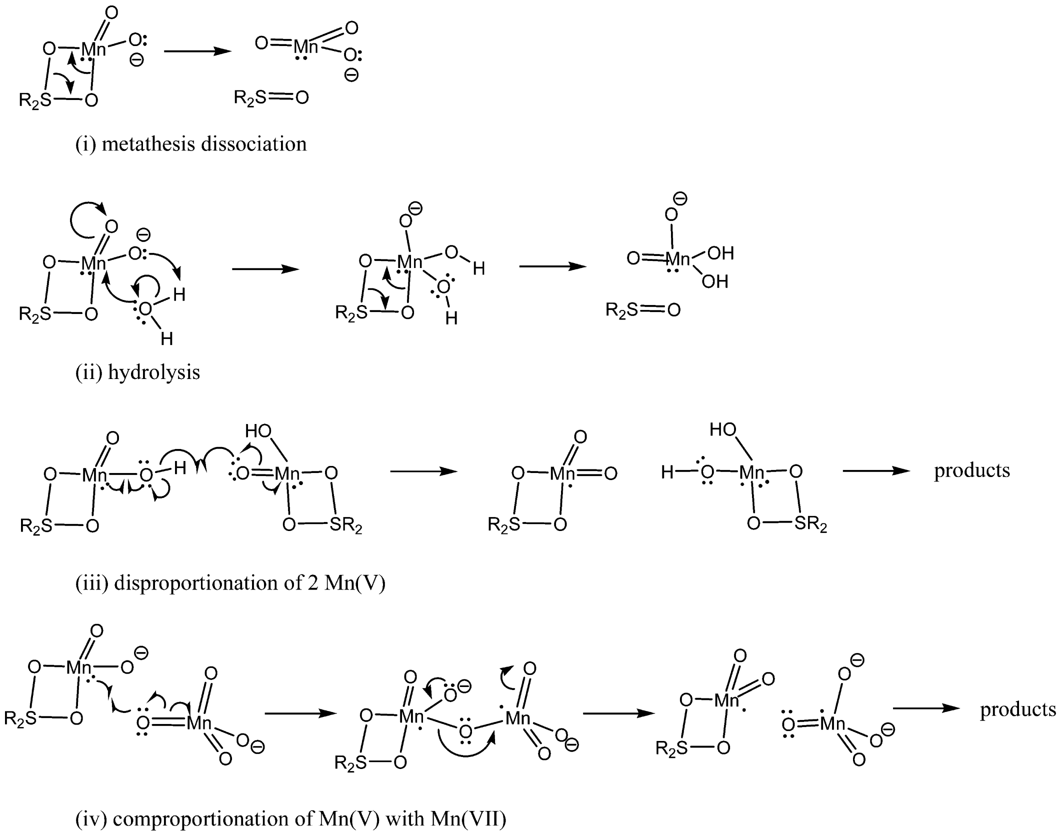

Figure 5. Hypothetical next steps for the cyclic intermediate.

might be expected from the bond lengths in the intermediate (Table 2). The computed thermodynamic data appear in Table 7.

Table 7. Calculated Energies (kJ mol^{-1}) of the Metathesis Dissociations[a]

compound	$\Delta^{\ddagger}E_{elec}$	$\Delta^{\ddagger}H_{298}$	ΔE_{elec}	ΔH_{298}
2a → **3a′**	34	30	−34	−33
2b → **3b′**	40	36	−29	−27
2c → **3c′**	36	33	−14	−12
5a → **6a′**	57	54	−53	−52
5b → **6b′**	57	54	−49	−47
5c → **6c′**	89	85	−13	−11

[a] CCSD/B1/PCM//B3LYP/B1 results with basis corrections added.

The activation barriers are larger than those for formation of the intermediate, which suggests that the cyclic intermediates would be detectable in an experiment. Since no such intermediate has been detected in experiments as far as we are aware, metathesis dissociation of the Mn(V) complex may *not* be the mechanism of intermediate breakup.

■ CONCLUSIONS

According to our calculations, permanganate oxidation of organic sulfides and sulfoxides proceeds via an initial 1,3-dipolar cycloaddition to a cyclic intermediate. This overturns previous ideas, and the analogy with ozonolysis and the permanganate oxidation of alkenes leads us to suggest that most organic oxidations by permanganate, and other oxyanions like periodate and perruthenate, occur via initial 1,3-dipolar cycloaddition. Direct Mn-atom interaction with the substrate, as Sharpless envisioned,[27] is unlikely to occur with MO_4^{n-} oxidations. Mn is merely the template for carrying nearly neutral O atoms to the reactive site.

The sulfur atom is both an electron-pair donor and an electron-pair acceptor, as would be expected of substrates for 1,3-dipolar cycloadditions. Since S—O bonds are polar, this results in a loss of net negative partial charge (i.e., an oxidation), which accumulates on the O atoms rather than Mn. The ab initio activation enthalpies are in reasonable agreement with the experimental data; the ab initio activation entropies are not, possibly because of problems with Eyring equation assumptions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Energies and Cartesian coordinates of all reported structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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