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Transition Structures of Epoxidation by $CH_3Re(O)_2(O_2)$ and $CH_3Re(O)(O_2)_2$ and Their Water Adducts

Yun-Dong Wu*,[†] and Jian Sun[†,‡]

Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, and Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, 610041, China

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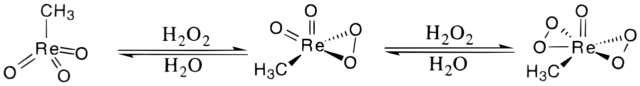
Methylrhenium trioxide (**1**, MTO) is one of the most versatile catalysts,[1] and its catalysis of alkene epoxidation has been studied extensively.[2−5] The active catalytic forms are **2**, **3**, and/or their water adducts.[6,7] In this paper, we report a theoretical study that addresses several important mechanistic aspects: (1) the relative reactivities of **2** and **3** toward alkenes, (2) the relative reactivities of the two oxygens of the peroxo group(s), (3) the detailed geometrical features of transition state of epoxidation,[3a,b] and (4) the effect of H_2O ligation on the reactivity.



1 **2** **3**

Geometries (Figure 1) were fully optimized with the density functional theory BLYP/HW3 method[8,9] using a GAUSSIAN 94 program.[10] Transition structures were confirmed by frequency calculations on the technetium congeners with the BLYP/3-21G method.[11]

The calculated geometry of **5** is very similar to the X-ray crystal structure.[2c] The two peroxo units are nearly coplanar with the methyl group. The calculated bond lengths are systematically longer than the experimental values by about 0.02−0.05 Å except for the Re−O(H2) bond which is longer by about 0.3 Å. We attribute this discrepancy to hydrogen bonding involving the water and diglyme in the crystal structure, which increases the donating ability of the oxygen.

In the monoperoxo structures (**2** and **4**), the η^2-O_2 unit is also nearly coplanar with the Re−C bond. One important difference between the monoperoxo and bisperoxo structures is in the $Re-O_a$ and $Re-O_b$ bond lengths. Although the two bond lengths are quite similar, the $Re-O_a$ bond in structures **2** and **4** is about 0.06 and 0.13 Å shorter than the $Re-O_b$ bond, respectively. On the other hand, the $Re-O_a$ bond in structures **3** and **5** is about 0.03 Å longer than the $Re-O_b$ bond, in agreement with the X-ray crystal structure.[2c] These indicate that the O_b in structures **2** and **4** might be intrinsically more reactive while the O_a might be more reactive in structures **3** and **5** (vide infra).

No π-complex can be located for ethene with **2**−**5**.[12] Instead, ethene directly approaches the Re−η^2-O_2 unit and forms a three-membered-ring transition structure. Each transition structure is in a spiro geometry.[13,14] We were unable to locate a planar transition structure.[13,15] The two carbon atoms of ethene and the η^2-O_2 unit are nearly in a plane. The O−O bond lengthens by about 0.3−0.4 Å. The nature of electrophilic addition by the peroxo group is indicated by charge transfer of about 0.3 units from ethene. Interestingly, the two forming O---C bonds are about 0.2 Å different in length in most structures. To test the significance of this distortion, **2A** and **2B** were optimized with the two C−O bonds at the same length. These symmetrical structures are higher in energy by within 0.4 kcal/mol. The above geometrical features, along with the calculated activation enthalpies (Table 1), are quite similar to those calculated for the epoxidation by dioxanes.[16]

The calculations give a 0.9 kcal/mol preference for **2A** over **2B** but a 2.5 kcal/mol preference for **4B** over **4A**. On the other hand, for the bisperoxo species **3** and **5**, the O_a is much more reactive than O_b toward the olefin. Thus, **3A** and **5A** are 7.2 and 6.0 kcal/mol more stable than **3B** and **5B**, respectively. Both geometrical factors and steric effects contribute to these interesting patterns of reactivity. Geometrically, the O_a-O_b in **2** are in such an environment that O_a is more strongly bound to Re than O_b, as indicated by the shorter $Re-O_a$ distance. Thus, O_b is intrinsically the better transferring oxygen. The steric effect, on the other hand, disfavors the attack of ethene on the O_b. In structure **2B**, two of the methyl hydrogens are about 2.2 Å away from the two "endo" hydrogens of ethene, respectively, causing severe steric interactions. Because of the two opposite effects, the calculations predict similar stabilities for transition structures **2A** and **2B**. The coordination of water in structure **4** has two important consequences: (1) the C−Re−O_b angle is opened up by about 3°. This results in reduced crowding in transition structure **4B**; (2) the $Re-O_b$ bond becomes considerably longer than the $Re-O_a$ bond, making O_b more reactive. Thus, **4B** is predicted to be more favorable

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[†] The Hong Kong University of Science and Technology.

[‡] Chinese Academy of Sciences.

(1) For recent reviews, see: (a) Remão, C. C.; Kühn, F. E.; Herrmann, W. A. *Chem. Rev.* **1997**, *97*, 3197. (b) Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169. (c) Herrmann, W. A. *J. Organomet. Chem.* **1995**, *500*, 149.

(2) (a) Herrmann, W. A.; Kratzer, R. M.; Fischer, R. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2652. (b) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243. (c) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157.

(3) (a) Al-Ajlouni, A. M.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 3969. (b) Al-Ajlouni, A. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1995**, *117*, 9243. (c) Zhu, Z.; Espenson, J. H. *J. Org. Chem.* **1995**, *60*, 7728.

(4) (a) Boehlow, T. R.; Spilling, C. D. *Tetrahedron Lett.* **1996**, *37*, 2717. (b) Murray, R. W.; Singh, M.; Williams, B. L.; Moncrieff, H. M. *Tetrahedron Lett.* **1995**, *36*, 2437. (c) Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 533.

(5) (a) Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189. (b) Copéret, C.; Adolfsson, H.; Sharpless, K. B. *Chem. Commun.* **1997**, 1565.

(6) Dickman, M. H.; Pope, M. T. *Chem. Rev.* **1994**, *94*, 569.

(7) Herrmann, W. A.; Correia, J. D. G.; Artus, G. R. J.; Fischer, R. W.; Romão, C. C. *J. Organomet. Chem.* **1996**, *520*, 139.

(8) (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785.

(9) The HW3 basis set is equivalent to the 6-31G* basis set, see: Johns, V.; Frenking, G.; Reetz, M. T. *Organometallics* **1993**, *12*, 2111.

(10) Gaussian 94, Revision B.3: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

(11) The transition structures for the Tc and Re systems are very similar.

(12) (a) Trost, M. K.; Bergman, R. B. *Organometallics* **1991**, *10*, 1172. (b) Mimoun, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 723.

(13) (a) Wu, Y. D.; Lai, D. G. W. *J. Am. Chem. Soc.* **1995**, *117*, 11327. (b) Wu, Y. D.; Lai, D. G. W. *J. Org. Chem.* **1995**, *60*, 673.

(14) (a) Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 10147. (b) Singleton, D. A.; Merrigan, S. R.; Liu, J.; Houk, K. N. *J. Am. Chem. Soc.* **1997**, *119*, 3385. (c) Bach, R. D.; Canepa, C.; Winter, J. E.; Blanchette, P. E. *J. Org. Chem.* **1997**, *62*, 5191. (d) Bach, R. D.; Winter, J. E.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1995**, *117*, 8586. (e) Yamabe, S.; Kondou, C.; Minato, T. *J. Org. Chem.* **1996**, *61*, 616. (f) Jørgensen, K. A. *Acta Chem. Scand.* **1992**, *46*, 82.

(15) Finn, M. G.; Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, p 247.

(16) (a) Jenson, C.; Liu, J.; Houk, K. N.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 12982. (b) Bach, R. D. Andrés, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207.

S0022-3263(98)00002-4 CCC: $15.00

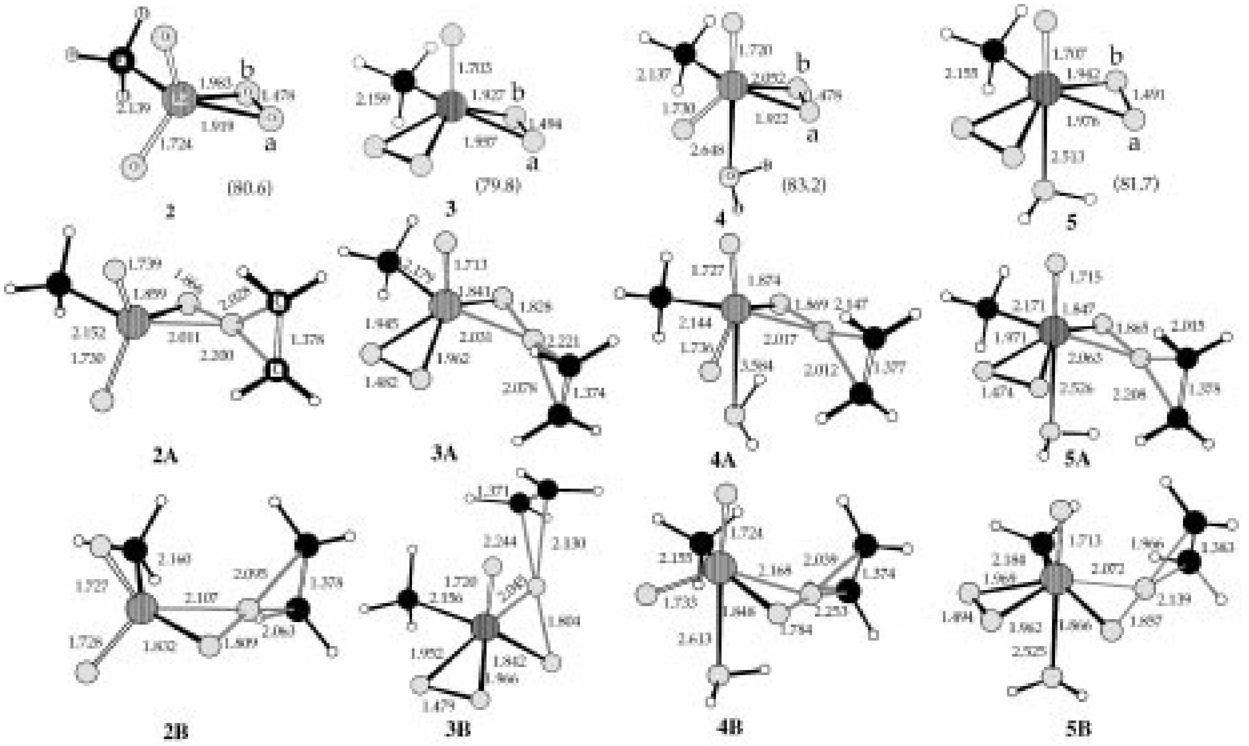

Figure 1. Calculated structures of monoperoxo- and bisperoxomethylrhenium trioxide and their H_2O adducts and the transition structures for the epoxidation of ethene with these oxidants. The values of angle C−Re−O_b in **2**−**5** are given in parentheses.

Table 1. Calculated Gas-Phase Reaction or Activation Enthalpy (kcal·mol^{-1})

	$\Delta H°$		$\Delta H°$
$\mathbf{1} + H_2O_2 \rightarrow \mathbf{2} + H_2O$	−3.0	$\mathbf{2} + H_2O_2 \rightarrow \mathbf{3} + H_2O$	1.0
$\mathbf{2} + H_2O \rightarrow \mathbf{4}$	−6.5	$\mathbf{3} + H_2O \rightarrow \mathbf{5}$	−13.9
$\mathbf{2} + CH_2{=}CH_2 \rightarrow \mathbf{2A}$	12.2	$\mathbf{3} + CH_2{=}CH_2 \rightarrow \mathbf{3A}$	6.6
$\mathbf{2} + CH_2{=}CH_2 \rightarrow \mathbf{2B}$	13.1	$\mathbf{3} + CH_2{=}CH_2 \rightarrow \mathbf{3B}$	13.8
$\mathbf{4} + CH_2{=}CH_2 \rightarrow \mathbf{4A}$	13.3	$\mathbf{5} + CH_2{=}CH_2 \rightarrow \mathbf{5A}$	10.4
$\mathbf{4} + CH_2{=}CH_2 \rightarrow \mathbf{4B}$	10.8	$\mathbf{5} + CH_2{=}CH_2 \rightarrow \mathbf{5B}$	16.4

than **4A** by over 2 kcal/mol. The situation for the bisperoxo species is different. In structure **3**, the O_b is in a better position to form a double bond with Re and the O_a is a better transferring group. Since the C−Re−O_b angle in **3** is even smaller than that in **2**, an even larger steric interaction would be expected for **3B**, as indicated by the ~30° distortion of the reactive η^2-O_2 unit in **3B**. Both the geometrical and steric factors disfavor the electrophilic attack of O_b to ethylene. The coordination of water in **5** has a similar effect as in **4**, but to a lesser extent.

Without water complexation, calculations indicate that the bisperoxo species **3** is much more reactive than the monoperoxo species **2** (by about 6.3 kcal/mol). This is due at least to two reasons: (1) in **2**, the reactive oxygen is O_b, and **2B** is severely destabilized by steric interactions, while for **3**, the reactive oxygen is O_a and the transition structure **3A** does not suffer from steric interaction; (2) the Re center is more acidic in **3** than in **2**. Thus, the O_a−O_b unit is more tightly bound in **3**, resulting in a weaker O_a−O_b bond and higher reactivity.

Calculations give a complexation enthalpy of −6.5 kcal/mol for **4** and −13.9 kcal/mol for **5**, indicating much stronger acidity for **3** over **2**. While the complexation of H_2O with **3** is apparently strong, in agreement with experiments,[2c,17,18] **4** is predicted to be unstable.[18,20] The water complexation in **5** reduces the Re−O_b binding and slightly shortens the O_a−O_b bond length. This reduces its reactivity, and **5A** and **5B** are computed to have 3.8 and 2.6 kcal/mol higher activation enthalpy than **3A** and **3B**, respectively, in accord with the experimental observation[2b] and calculation[21] that amine coordination reduces the reactivity of **3**. This effect is smaller for **4** and compensated by the favorable geometrical effects aforementioned in **4B**.

In summary, transition structures of epoxidation of ethene by **2**− **5** have been located. Each transition structure is in a spiro geometry. The two peroxo oxygens have different reactivities: For **4**, the oxygen adjacent to the methyl group is more reactive, while the oxygen that is away from the methyl is more reactive for the other species. It is predicted that **3** is much more reactive than **2**, and its reactivity is reduced by water complexation. We are currently studying a more detailed mechanism in an effort to understand the unusual pyridine acceleration effect found by Sharpless[5] and to design ligands for possible stereoselective version of reaction.

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(17) Herrmann, W. A.; Correia, J. D. G.; Kühn, F. E.; Artus, G. R. J.; Romão, C. C. *Chem. Eur. J.* **1996**, *2*, 167.

(18) The calculated complexation entropies for **2** + H_2O and **3** + H_2O are −37.8 and −37.7 eu, respectively. If the loss of entropy in solution is corrected to be −27.3 and −27.2 eu, respectively, according to the free-volume theory,[19] the calculated complexation free energy would be 1.6 and −5.8 kcal/mol for the two reactions.

(19) Benson, S. W. *The Foundations of Chemical Kinetics*; Krieger, Florida, 1982.

(20) (a) Abu-Omer, M. M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966. (b) Yamazaki, S.; Espenson, J. H.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4683.

(21) Sun, J.; Wu, Y.-D. Unpublished results.