

FORMATION OF HYDROPEROXIDE FROM SINGLET OXYGEN AND PROPENE: A DUALITY OF MECHANISMS BY PM3

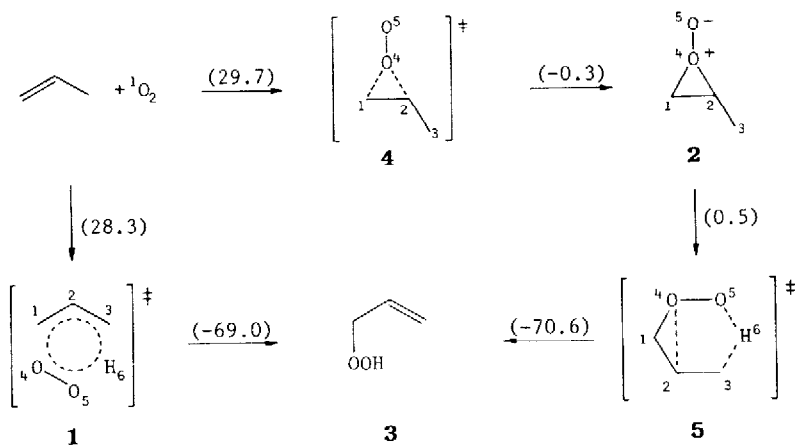
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Summary: Two alternative reaction pathways, one involving a concerted 6-membered ring transition state, the other, a loosely-bound peroxide intermediate, have been located on the PM3 semi-empirical potential energy surface for the reaction of singlet oxygen with propene. The calculations suggest that the former pathway is preferred by 1.4 kcal.mol⁻¹.

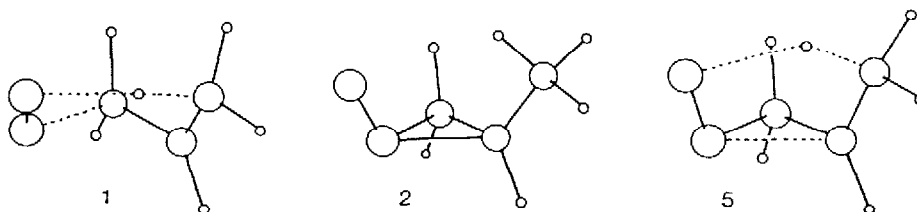
The reaction of appropriately substituted olefins with singlet (¹Δ_g) oxygen is a useful method of preparing allylic hydroperoxides. Although the reaction has been studied for some four decades, there is still some ambiguity concerning the mechanistic details.² Some authors have postulated a concerted mechanism proceeding via a 6-membered ring transition state³ (1), whereas others believe that the reaction proceeds via a peroxide intermediate⁴ (2), which might exist as a loosely-bound complex, and which subsequently rearranges to the hydroperoxide (3).

Theoretical approaches to this problem have been limited, with MINDO/3 favouring a peroxide intermediate⁵, while others suggest that a biradical pathway might be feasible.⁶ The



Relative energies in parentheses (kcal/mol).

Figure. Ball and Stick Representations of Structures **1**, **2** and **5**.



highest level calculations so far, however, discount this radical path, putting it some 5 kcal.mol⁻¹ above that for the perepoxide.⁷ It is interesting to note that the concerted transition state (**1**) remains conspicuously absent in the theoretical approaches.

We report that the new PM3 semi-empirical molecular orbital method⁸ suggests that both **1** and **2** lie on feasible alternative pathways on the potential energy surface.

All calculations were performed at the Restricted Hartree- Fock (RHF) level using the MOPAC version 5.0 molecular orbital package⁹ on a VAX 6310 computer. Structures were optimized to minima using the Broyden-Fletcher-Goldfarb-Shanno (BFGS)¹⁰ method or to transition states as described by Dewar and co-workers¹¹ and proven as corresponding to the appropriate stationary point by evaluation of the complete set of harmonic force constants in each case.

The PM3 calculations suggest that the pathway of lower energy is that which proceeds via the concerted transition state (**1**), but the transition state (**4**) leading to the perepoxide (**2**) is calculated to be only 1.4 kcal.mol⁻¹ higher in energy. In fact, **2** is predicted to lie in a very shallow well, only 0.3 kcal.mol⁻¹ below **4** and only 0.5 kcal.mol⁻¹ below the transition state (**5**) to the hydroperoxide (**3**).

It is interesting to note that while PM3 suggests a duality of mechanisms, AM1¹² suggests that **3** is formed exclusively via **1**. Indeed, no structure resembling the perepoxide (**2**) could be located on the AM1 potential energy surface. In contrast, MNDO predicts exclusive formation of **3** in a mechanism involving a number of (asynchronous) steps. The AM1 and MNDO results are not unexpected as MNDO is known to favour asynchronous pathways,¹³ while AM1 tends to prefer synchronicity.¹⁴

The Table lists the principal features of the geometries of **1**, **2**, **4** and **5**, their heats of formation and imaginary frequencies (where appropriate) as calculated by PM3 and the structures of **1**, **2** and **5** are illustrated in the Figure. It is clear that **1** is an "early" transition state, with

Table. Major Geometric Features,^a Heats of Formation^b and Imaginary Frequencies^c (where appropriate) of Structures **1**, **2**, **4** and **5** as calculated by PM3 (AM1 data in parentheses).

Variable	Structure			
	1	2	4	5
r(C ₁ C ₂)	1.414 (1.458)	1.458	1.428	1.442
r(C ₁ O ₄)	1.635 (1.607)	1.559	1.643	1.562
r(C ₂ C ₃)	1.414 (1.425)	1.483	1.478	1.456
r(C ₂ O ₄)	2.276 (2.296)	1.664	1.809	1.877
r(C ₃ H ₆)	1.189 (1.267)	-	-	1.147
r(O ₄ O ₅)	1.261 (1.182)	1.272	1.242	1.269
r(O ₅ H ₆)	1.695 (1.553)	-	-	1.831
θ(C ₁ C ₂ C ₃)	118.3 (117.8)	121.0	121.4	118.3
θ(C ₁ C ₂ O ₄)	45.4 (43.8)	59.5	59.6	54.2
θ(C ₂ C ₁ O ₄)	96.3 (98.2)	-	-	-
θ(C ₂ C ₄ C ₅)	-	118.1	117.5	-
θ(C ₂ C ₃ H ₆)	100.9 (100.3)	-	-	104.1
θ(C ₁ O ₄ O ₅)	115.3 (116.1)	-	-	114.9
ω(C ₃ C ₂ C ₁ O ₄)	76.1 (69.0)	-	-	89.0
ω(C ₃ C ₁ C ₂ O ₄)	-	105.2	101.4	-
ω(C ₁ C ₂ C ₃ H ₆)	59.5 (56.2)	-	-	57.6
ΔH _f	53.1 (45.0)	54.2	54.5	54.7
v	604 (1379)	-	357	80

a. Distances(r) in Å, angles(θ) and dihedral angles(ω) in degrees. b. ΔH_f in kcal.mol⁻¹. c. Imaginary frequencies (in cm⁻¹).

relatively long forming bonds (r(C₃O₄) = 1.635Å; r(O₅H₆) = 1.695Å) and short breaking bonds (r(C₁H₆) = 1.189Å). This is in agreement with Nickon and co-workers³ suggestion of an "early" concerted transition state to accommodate their experimental findings.

PM3 also suggests that the peroxide (**2**) is loosely-bound, in agreement with the conclusions of a number of workers,⁴ as is evident from the low barrier to rearrangement and relatively long bonds (r(C₁O₄) = 1.559Å; r(C₂O₄) = 1.664Å). The final transition state (**5**) is once again "early" and easily achieved due to the *cis* orientation¹⁵ of groups in **2**, as is depicted in the Figure.

PM3 is a relatively new method and work so far⁸ suggests that it is superior to the older methods based on the NDDO (Neglect of Differential Diatomic Overlap) approximation, namely AM1 and MNDO. PM3 results have been compared with those of the correlated⁸ *ab initio*

(MP2/3-21G) method.¹⁶ This would suggest that the PM3 data are reliable and that under non-polar or gas-phase conditions, **3** is formed via **1**. As the energy difference between **1** and **4** is small, solvent may be expected to play an important role. Polar solvents may favour the peroxide pathway, as has been suggested by Jefford and co-workers,¹⁷ who propose a solvent-dependent change of mechanism to explain their results.

Further work will be presented in due course and we thank the Birkbeck College Computer Centre for time on the VAX 6310 computer.

Notes and References

1. Ramsay Memorial Research Fellow.
2. See: A.A. Frimer, L.M. Stephenson in *Singlet O₂ Vol II: Reaction Modes and Products*, Part I, CRC Press, Boca Raton, Fla. (1985); K. Gollnick, H.J. Kuhn in *Singlet Oxygen*, H.H. Wasserman, R.W. Murray Ed., Academic Press, N.Y. (1979).
3. A. Nickon, V.T. Chuang, P.J.L. Daniels, R.W. Denny, J.B. DiGiorgio, J. Tsunetsugu, H.G. Vilhuber, E. Werstiuk, *J.Am.Chem.Soc.*, **94**, 5517 (1972).
4. J.R. Hurst, S.L. Wilson, G.B. Schuster, *Tetrahedron*, **41**, 2191 (1985); M. Orfanopoulos, C.S. Foote, *J.Am.Chem.Soc.*, **110**, 6583 (1988); R. Matusch, G. Schmidt, *Angew.Chem.Int.Ed.Engl.*, **27**, 717 (1988); L.M. Stephenson, M.J. Grdina, M. Orfanopoulos, *Acc.Chem.Res.*, **13**, 419 (1980); A.A. Frimer, P.D. Bartlett, A.F. Boschung, J.G. Jewett, *J.Am.Chem.Soc.*, **99**, 7977 (1977).
5. M.J.S. Dewar, W. Thiel, *J.Am.Chem.Soc.*, **97**, 3978 (1975).
6. K. Yamaguchi, S. Yabushita, T. Fueno, K.N. Houk, *J.Am.Chem.Soc.*, **103**, 5043 (1981).
7. M. Hotokka, B. Roos, P. Siegbahn, *J.Am.Chem.Soc.*, **105**, 5263 (1983).
8. The Neglect of Differential Diatomic Overlap (NDDO) approximate molecular orbital method has to date been parameterized three times. The first resulted in the MNDO method, the second in the AM1 (Austin Model 1) method and the third in the PM3 (Parametric Method 3) method. For a description of PM3, see: J.J.P. Stewart, *J.Comput.Chem.*, **10**, 209 (1989); J.J.P. Stewart, *J.Comput.Chem.*, **10**, 221 (1989).
9. Available through the Quantum Chemistry Program Exchange, University of Indiana, as QCPE no. 455.
10. C.G. Broyden, *J.Inst.Math.Appl.*, **6**, 222 (1970); R. Fletcher, *Comput.J.*, **13**, 317 (1970); D. Goldfarb, *Math.Comput.*, **24**, 23 (1970); D.F. Shanno, *Math.Comput.*, **24**, 647 (1970).
11. M.J.S. Dewar, E.F. Healy, J.J.P. Stewart, *J.Chem.Soc., Faraday Trans. 2*, **80**, 227 (1984).
12. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, *J.Am.Chem.Soc.*, **107**, 3902 (1985).
13. M.J.S. Dewar, S. Olivella, J.J.P. Stewart, *J.Am.Chem.Soc.*, **108**, 5771 (1986).
14. D.K. Agrafiotis, H.S. Rzepa, *J.Chem.Soc., Chem. Commun.*, 902 (1987).
15. An alternative peroxide of *trans* stereochemistry can be envisaged. This structure, however, cannot lie on the path to the hydroperoxide (**3**).
16. P.A. Hunt, H.S. Rzepa, *J.Chem.Soc., Chem. Commun.*, 623 (1989).
17. C.W. Jefford, S. Kohmoto, *Helv.Chim.Acta.*, **65**, 133 (1982)

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