

## Electronic Supplemental Information

### Formation of persulphate from sodium sulphite and molecular oxygen catalysed by $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ - aerobic epoxidation and hydrolysis

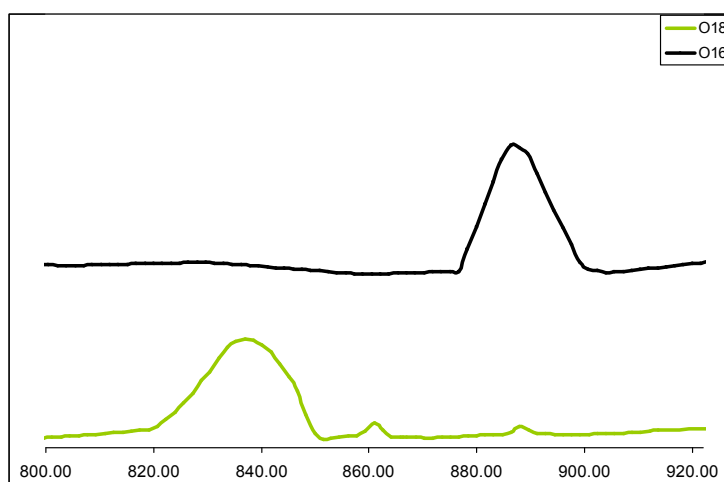
#### Experimental Details.

**Materials:** Solvents and substrates available from commercial sources were of the highest purity available and were used without further purification. Alkenes were purified on a neutral alumina column in order to remove peroxides and other impurities. N-tert-butyl-alpha-phenylnitron was purified on an activated carbon column to remove paramagnetic impurities.  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$  was prepared according to a literature method.<sup>1</sup> Sodium sulphite (98%) was purchased from Sigma-Aldrich.

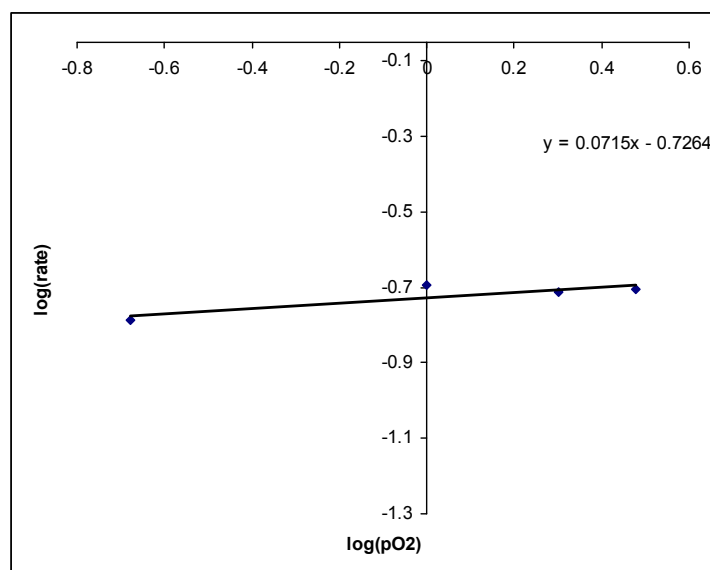
**Instruments:** The IR spectra were measured on a Nicolet 6700 FTIR using KBr pellets. EPR spectra were recorded on a Bruker ELEXSYS 500 X-band spectrometer equipped with a Bruker ER4102ST resonator in a J-young 3 mm tube at room temperature. The EPR spectra were simulated with home written Matlab program using EasySpin subroutines.<sup>1</sup> Raman spectra were acquired on Renishaw Micro Raman In Via Imaging Microscope using a 633 nm laser. Samples were obtained by evaporation of the solvent. UV-Visible spectra were measured on Agilent 89090A spectrophotometer using 1.0 cm quartz cuvettes at the given concentrations.

**Oxidation reactions:** Catalytic oxidation reactions were carried out in 25 mL ace glass pressure tubes. The tubes were charged with the catalyst, sodium sulphite, substrate and solvent in the specified amounts; air was purged and then pressurized with  $\text{O}_2$  and heated in a temperature controlled oil bath. At each relevant time period, a 50  $\mu\text{L}$  aliquot was taken, dissolved in 0.2 mL DCM and then analyzed by GC-FID/GC-MS. The separation was carried out using a 5% phenylmethylsilicone 0.32 mm i.d., 0.25  $\mu\text{m}$  coating, 30 m long column using He as eluent.

**Figure S1:** Raman spectra obtained by mixing  $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ , sodium sulphite and  $^{16}\text{O}_2$  (black trace) /  $^{18}\text{O}_2$  97% (green trace) 1 bar in AcOH at 65 °C. small impurities, <2% are observable.



**Figure S2:** Rate of cyclododecene epoxidation as a function of O<sub>2</sub> pressure. Cyclododecene (0.43 mmol), Na<sub>2</sub>SO<sub>3</sub> (0.43 mmol), 1 mol % H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (4.3 μmol) in 1 mL AcOH, O<sub>2</sub> pressure (0.21-3 bar), 110 °C.



1. G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.* 1968, 7, 437-441.
2. <http://www.easyspin.org/>