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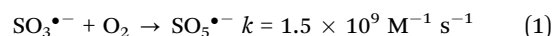
Formation of persulphate from sodium sulphite and molecular oxygen catalysed by $H_5PV_2Mo_{10}O_{40}$ – aerobic epoxidation and hydrolysis†

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The $H_5PV_2Mo_{10}O_{40}$ polyoxometalate catalysed the electron transfer oxidation of sulphite to yield a sulphite radical, $SO_3^{\bullet-}$ that upon addition of O_2 yielded a peroxosulphate species efficient for the $H_5PV_2Mo_{10}O_{40}$ catalysed epoxidation of alkenes. The acidic polyoxometalate further catalysed hydrolysis of the epoxide to give vicinal diols in high yields.

Epoxidation of alkenes and subsequent transformations, for example, acid catalysed hydrolysis to vicinal diols is a central transformation in synthetic organic chemistry. By far the most common method to effect this transformation is with peroxides with recent emphasis on H_2O_2 .¹ These peroxide species can be formed *in situ* using molecular oxygen and the combination of aldehydes and O_2 appears to be the most reported procedure, releasing a carboxylic acid as co-product.² Inorganic peroxides, most notably the persulphate anion, HSO_5^- , which is available as a triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ is also an efficient oxidant.³ Although commercially available, it contains only ~50 wt% oxidant and is prepared from concentrated H_2O_2 , oleum or sulphuric acid and an alkali potassium compound.⁴ It would appear to be enticing to prepare a persulphate oxidant in an aerobic procedure using sodium sulphite, which is readily available from SO_2 scrubbing with sodium carbonate as part of flue gas desulphurization processes.⁵

Sodium sulphite, Na_2SO_3 , has a redox potential of $E^0 = -0.6$ V versus SCE at pH = 3.6.⁶ Thus, it has a propensity to act as a reducing agent and indeed its chemical oxidation to yield the sulphite radical anion has been reported with radicals such as OH^\bullet , NH_2^\bullet and others,⁷ and with oxidizing transition metals such as Ce^{IV} ,⁸ Mn^{III} ,⁹ and Fe^{III} .¹⁰ Photolytic oxidation has also been reported.¹¹ The free sulphite radical anion is known to recombine very rapidly with oxygen according to eqn (1).¹²

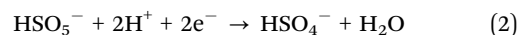


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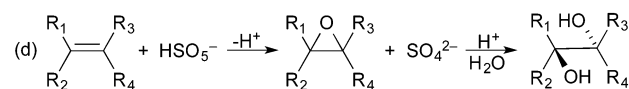
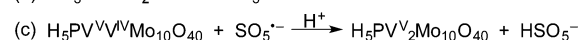
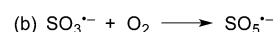
The peroxomonosulphate radical anion $SO_5^{\bullet-}$, that is formed, can act as an oxidant; $E^0 = 0.86$ V versus SCE.⁷ The product of this one-electron reduction is SO_5^{2-} , with a two-electron redox potential of $E^0 = 1.58$ V versus SCE, eqn (2), which explains its high activity in oxidation reactions.³



Surprisingly, there have been only a couple of reports on the use of SO_3^{2-}/O_2 for the *in situ* formation of HSO_5^- , notably in biomimetic oriented research using iron and manganese porphyrins.¹³ The polyoxometalate, α - $H_5PV_2Mo_{10}O_{40}$, has been utilized in many aerobic catalytic oxidation reactions that are initiated by an electron transfer step from a substrate to $H_5PV_2Mo_{10}O_{40}$; catalytic cycles can be completed with O_2 .¹⁴ Therefore, a strategy for a simple and robust catalytic oxidation of alkenes with SO_3^{2-}/O_2 catalysed by $H_5PV_2Mo_{10}O_{40}$ is proposed according to Scheme 1. The acidic polyoxometalate can also catalyse the hydrolysis of epoxides to vicinal diols.

The feasibility of electron transfer, Scheme 1, step a, from the sulphite anion to the polyoxometalate was assessed by reacting $H_5PV_2Mo_{10}O_{40}$ with an excess Na_2SO_3 in acetic acid under argon. The typically orange-red coloured solution of oxidized $H_5PV_2Mo_{10}O_{40}$ turned green after the addition of Na_2SO_3 with the signature absorption band of the reduced polyoxometalate, Fig. 1.

Further speciation of the intermediates formed was carried out by EPR spectroscopy. Fig. 2 shows an eight line isotropic spectrum attributable to a V^{IV} ($I = 7/2$) containing polyoxometalate¹⁵ and a



Scheme 1 Epoxidation/hydrolysis of alkenes by SO_3^{2-}/O_2 catalysed by $H_5PV_2Mo_{10}O_{40}$.

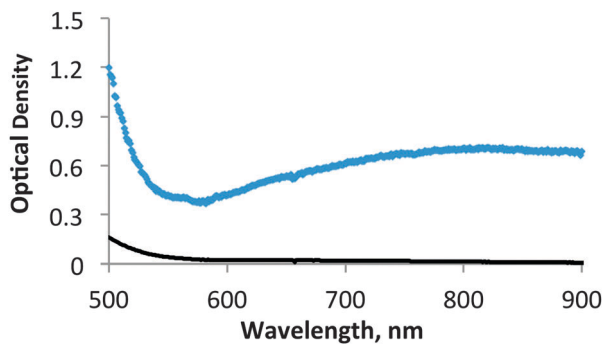


Fig. 1 Visible spectra of 1 mM $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ before (black line) and after reaction (blue line) with a twenty fold excess of Na_2SO_3 under Ar at 295 K for 1 h.

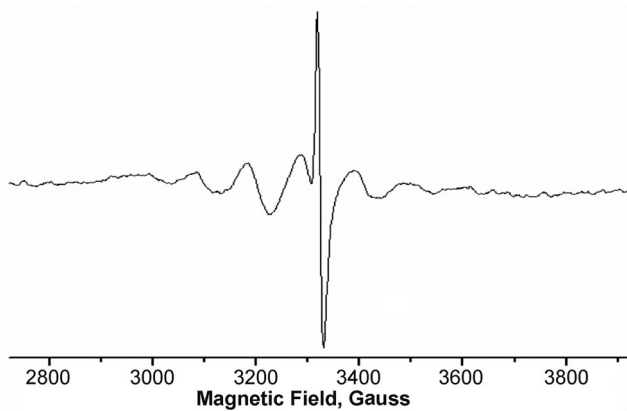


Fig. 2 EPR spectrum of 4.26 mM $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ reacted with 0.426 M Na_2SO_3 dissolved in 1 mL AcOH under Ar at 295 K for 1 h; measured at 295 K.

sharp peak at $g = 2.0145$ that is assigned to the sulphite radical anion.

The assignment of the sulphite radical anion was confirmed by addition of the *N-tert-butyl-alpha-phenylnitron* (PBN) spin trap that yielded the expected 6 line spectrum, Fig. 3, verified by simulation and is in accordance to the literature values.¹⁶

To demonstrate the formation of persulphate, Scheme 1, steps b and c, 4.3 μmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ was reacted with 0.43 mmol Na_2SO_3 in 1 mL AcOH under 1.5 bar O_2 . The peroxy O–O bond of peroxomonosulphate anion, SO_5^{2-} was observed by Raman spectroscopy with an absorption peak at 886 cm^{-1} , which is in accordance to the literature values.¹⁷ The expected isotope shift for ^{18}O – ^{18}O using $^{18}\text{O}_2$ (97%) was observed at 837 cm^{-1} (Fig. S1, see ESI†).

Having observed the expected reaction intermediates as hypothesized in Scheme 1, the catalytic oxidation of alkenes with $\text{Na}_2\text{SO}_3/\text{O}_2$ catalysed by $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ was pursued, Table 1.

As one can see from the results, internal alkenes reacted very efficiently with excellent total product yields, >95%, based on both the alkene and Na_2SO_3 after 4 h at 110 °C. The initially formed epoxide is mostly hydrolysed to the corresponding *trans*-diol; notably no acetate esters were observed. For cyclic alkenes, high yields, ~90%, based on both the alkene and Na_2SO_3 were

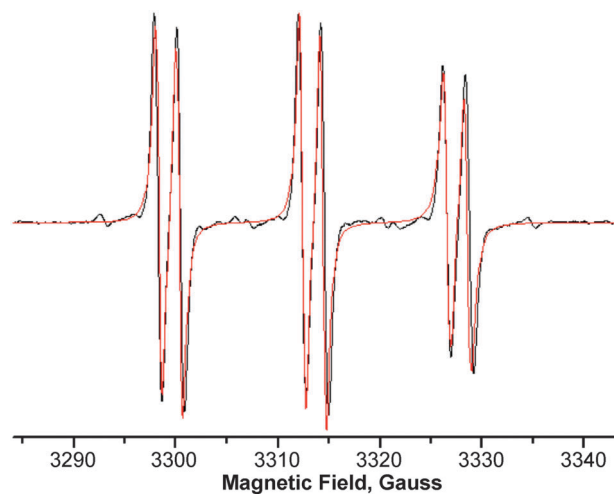


Fig. 3 Experimental EPR spectrum (black) of 4.26 mM $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ mixed with 0.0426 M Na_2SO_3 and 0.0852 M *N-tert-butyl-alpha-phenylnitron*, dissolved in 1 mL AcOH under argon at 295 K for 1 h; measured at 295 K. Simulated spectrum (red). $A_N = 14.3\text{ G}$, $A_H = 2.0\text{ G}$.

Table 1 Catalytic epoxidation/hydrolysis of representative alkenes

Substrate	Time (h)	TON	Epoxide (%)	Diol (%)
Cyclooctene	15	89	94	0 ^a
Cyclododecene	1 (4) ^b	25 (91)	99 (70)	0 (8) ^c
5-Decene	1 (4) ^b	20 (97)	92 (6)	8 (94)
4-Octene	1 (4) ^b	18 (95)	87 (11)	13 (89)
Methyloleate	1	20	88	0 ^d
1-Octene	1 (11)	10 (27)	85 (7)	15 (93)
1-Nonene	1 (11)	11 (28)	90 (11)	10 (89)
1-Decene	1 (11)	10 (29)	91 (16)	9 (84)
1-Octene ^e	11	94	15	85
1-Nonene ^e	11	87	13	87
1-Decene ^e	11	91	6	94

Reaction conditions: substrate (0.43 mmol), Na_2SO_3 (0.43 mmol), 1 mol% $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (4.3 μmol), 1 mL AcOH, 1 bar O_2 , 65 °C. ^a 6% 1,3-cyclododecene was formed. ^b After 1 h the reaction was heated to 110 °C. ^c 12% 1,3-cyclododecene was formed. ^d 2% diene was formed. ^e 0.946 mmol Na_2SO_3 added in portions – 0.086 mmol h^{-1} .

also observed. For these substrates the hydrolysis to diol was quite slow and more minimal. Primary alkenes reacted more sluggishly with conversions of only ~30% after 11 h. However, if the oxidation of primary alkenes was carried out by addition of Na_2SO_3 in small portions (Table 1 last three entries) then high conversions and very good yields of diols can also be attained with only a 2.2 fold excess of Na_2SO_3 . Initially formed epoxides are hydrolysed to the diols and here also no acetate esters were noted. The higher reactivity of internal *versus* primary alkenes suggests that the rate determining step of the entire reaction sequence, Scheme 1, is the oxygen transfer (epoxidation) step from an electrophilic oxidant to a nucleophilic alkene. This is supported by the observation that no reduced polyoxometalate was observed during the aerobic reaction and that the reaction rate is zero order in O_2 , Fig. S2 (ESI†). It is important to note that the sodium sulphate by-product formed in the reaction precipitates from the reaction mixture and can easily be filtered off from the organic reaction mixture.

An experiment using the non-acidic $((\text{C}_4\text{H}_9)_4\text{N})_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, yielded little product presumably due to its lower oxidation potential *versus* $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$.¹⁸ The effect of the presence of vanadium in the polyoxometalate was evaluated by comparing reactivity of $\text{H}_{3+x}\text{PV}_x\text{Mo}_{12-x}\text{O}_{40}$ for $x = 0, 1,$ and 2 in the catalytic epoxidation of cyclododecene. The reaction conditions were 0.43 mmol cyclododecene, 0.0043 mmol polyoxometalate (1 mol%), 0.43 mmol Na_2SO_3 at 65 °C in 1 mL AcOH under 2 bar O_2 , 1 h. The relative efficiency as measured by the turnover number was $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ (58) > $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ (19) > $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (3), resembling the order found for other reactions catalysed by phosphovanadomolybdates and is explained by the activity for electron transfer oxidation: $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ > $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ > $\text{H}_3\text{PMo}_{12}\text{O}_{40}$.¹⁴ Above it was shown by Raman spectroscopy that peroxosulphate species were formed. A reaction carried out with $^{18}\text{O}_2$ (4.3 μmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$, 0.43 mmol Na_2SO_3 , 0.43 mmol *cis*-cyclooctene, 65 °C in 1 mL AcOH, 1.5 bar 97% $^{18}\text{O}_2$) yielded >95% 18-O labelled *cis*-cyclooctene oxide, indicating that the persulphate intermediate formed is also the oxygen donor.

In summary, a protocol has been developed for the *in situ* formation of monooxygen persulphate from inexpensive $\text{Na}_2\text{SO}_3/\text{O}_2$ using an inorganic polyoxometalate $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ catalyst. The reaction sequence, Scheme 1, has been delineated and oxygen transfer to some representative alkenes has been quantified. The insolubility of the by-product, Na_2SO_4 , makes this protocol a good alternative to the aldehyde/ O_2 method often used for *in situ* peracid formation.‡ Future research will expand the reaction scope to additional substrate types.

Notes and references

‡ Specifically $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ did not catalyse the epoxidation of cyclododecene with isobutyraldehyde/ O_2 , that is 0.43 mmol cyclododecene, 0.0043 mmol $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ and 0.43 mmol $(\text{CH}_3)_2\text{CHCHO}$ at 65 °C in 1 mL AcOH or CH_3CN under 2 bar O_2 for 1 h yielded no product.

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