Transition Metal Substituted Keggin Type Polyoxomolybdates as Bifunctional Catalysts for the Epoxidation of Alkenes by Molecular Oxygen

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In a one-pot reaction, transition metal substituted polyoxomolybdates are shown to be bifunctional catalysts for epoxidation of alkenes by *via* oxygen transfer from intermediate alkylhydroperoxides; the latter being formed by catalytic autoxidation with molecular oxygen.

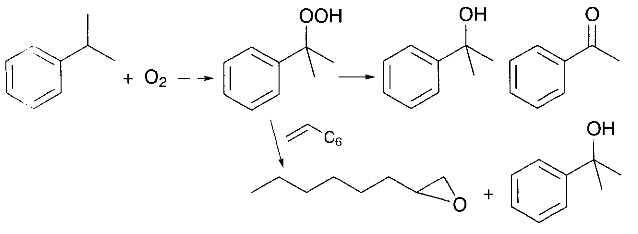
The use of molecular oxygen in the liquid-phase synthesis of organic compounds is limited because its triplet ground precludes reaction with singlet organic compounds. Therefore, molecular oxygen is often used in free radical autoxidation reactions as in the indirect epoxidation of alkenes.[1] Thus, aldehydes and alkanes may be autoxidized to peracids and alkylhydroperoxides, eqn. (1), which can be then used as oxygen transfer agents in the epoxidation of alkenes, eqn. (2).

$$\mathrm{RCHO\ or\ RH + O_2 \rightarrow RCOOOH\ or\ ROOH} \qquad (1)$$

$$\mathrm{RCOOOH\ or\ ROOH + R'CH{=}CHR'' \rightarrow RCOOH\ or\ ROH + R'CH(O)CHR''} \qquad (2)$$

Although conceptually, there is no difference in use of aldehydes or alkanes to 'activate' molecular oxygen, there are important chemical differences between the two. First, autoxidations of aldehydes are generally faster by at least two orders of magnitude than those of alkanes.[2] Second, alkenes can be epoxidized non-catalytically by peracids whereas for hydroperoxides there are only catalytic procedures usually based on high-valent d^0 transition metal *e.g.* Ti^{IV}, V^{V}, Mo^{VI} or W^{VI} compounds.[3] Importantly, catalysts common in autoxidations, *e.g.* Co$^{II/III}$ and/or Mn$^{II/III}$, also catalyse the homolytic decomposition of hydroperoxides to alcohols and/or ketones *via* the well known Haber–Weiss mechanism. These distinctions have been translated into two different synthetic procedures. Thus, there are many examples (also with polyoxometalates)[4] of one-pot procedures where aldehydes and alkenes are mixed with molecular oxygen in the presence of catalysts to yield epoxides. On the other hand, only two-stage procedures are common when using alkanes *i.e.* first formation and isolation of the intermediate hydroperoxide and then epoxidation in a separate step as in the manufacture of propylene oxide from isobutane, propylene and molecular oxygen.[1]

Here we report on the use of transition metal substituted Keggin type polyoxometalates (TMSP) of the general formula, P(TM)M$_{11}$O$_{39}^{q-}$ where TM = Co^{II}, Mn^{II}, Ru^{III} and M = Mo^{VI} W^{VI}, as catalysts for the combined one stage autoxidation of alkanes and the epoxidation of alkenes, eqns. (1) and (2). The coexistance of a transition metal centre of high oxidation potential as an autoxidation catalyst along with a polyoxometalate cluster or ligand as an epoxidation catalyst[5] allows such compounds to be effective bifunctional catalysts provided the rates of autoxidation and epoxidation are compatible. The TMSP compounds were prepared according to the known literature procedures[6] except for PRu^{III}Mo$_{11}$O$_{39}^{4-}$† which is only now reported. In a typical reaction, Scheme 1, 1 mmol cumene as a representative alkane, 1 mmol oct-1-ene as a representative alkene and 1 µmol (0.1 mol%) TMSP as tetrabutylammonium salt were dissolved in 1 ml acetonitrile as solvent and heated at 80 °C for 24 h under 1 atm molecular oxygen in a hermetically sealed 3 ml vial, Fig. 1.



Scheme 1

Alternatively the catalytic bifunctionality of the TMSP compounds can be observed by use of cyclohexene as single substrate (reactions were carried out as above at 60 °C), Fig. 2, where initial autoxidation yields cyclohexene hydroperoxide which can then form cyclohexene oxide and cyclohexen-2-ol *via* oxygen transfer or cyclohexen-2-ol and cyclohexen-2-one by decomposition, Scheme 2. In this manner, the ratio cyclohexene oxide to cyclohexen-2-ol and cyclohexen-2-one products are a measure of the effectivity of the TMSP compounds as bifunctional catalysts.

The results (Figs. 1, 2)‡ show that there are significant differences between the polyoxomolybdates and polyoxotungstates with more subtle differences between the various

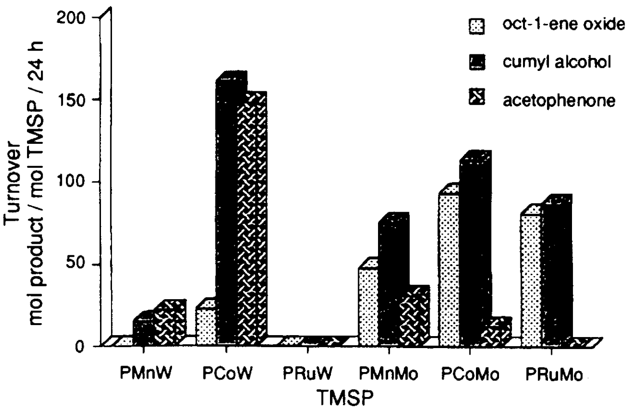


Fig. 1 The one stage oxidation of cumene and oct-1-ene catalysed by various TSMP. Reaction conditions: 1 mmol cumene, 1 mmol oct-1-ene and 1 µmol (0.1 mol%) TMSP as tetrabutylammonium salt in 1 ml acetonitrile, 80 °C, 24 h, 1 atm molecular oxygen.

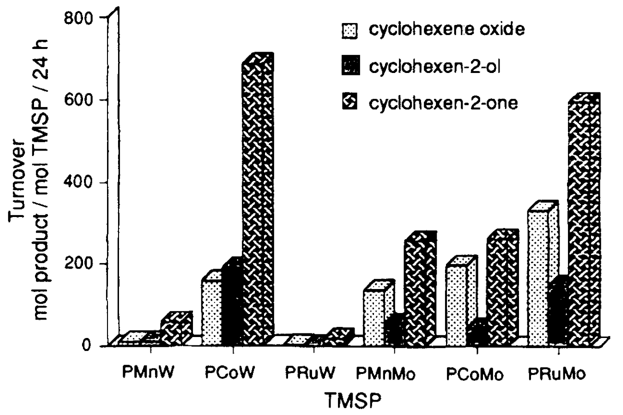
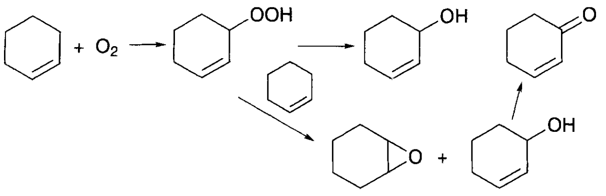


Fig. 2 The oxidation of cyclohexene catalysed by various TSMP. Reaction conditions: 1 mmol cyclohexene and 1 µmol (0.1 mol%) TMSP as tetrabutylammonium salt in 1 ml acetonitrile, 80 °C, 24 h, 1 atm molecular oxygen.

substituted transtion metals. In the case of the polyoxomolybdates, the low ratios of cumyl alcohol to oct-1-ene *oxide* (PMnMo, 1.56; PCoMo, 1.21; PRuMo, 1.07) and cyclohexen-2-ol and cyclohexen-2-one to cyclohexene oxide (PMnMo, 2.3; PCoMo, 1.5; PRuMo, 2.2) indicate that the rates of hydroperoxide formation and epoxidation are well correlated with less significant formation of decomposition products including acetophenone. Especially noteworthy is the PRuMo catalyst in the cumene/oct-1-ene system. The polyoxotungstates, on the other hand were found to be basically only effective as autoxidation catalysts showing only small amounts of oxygen transfer products. Thus, in the oxidation of cumene/oct-1-ene, acetophenone was the major product and even trace amounts of oct-1-en-3-ol and oct-1-en-3-one could be observed by GC–MS. In the case of cyclohexene as substrate ratios of cyclohexen-2-ol and cyclohexen-2-one to cyclohexene oxide varied between 5.5 to 6.4 which are typical values for the autoxidation of cyclohexene. The cobalt substituted compound is by far the most reactive with the manganese and ruthenium analogues showing little or almost no activity.

The success of the polyoxomolybdates as bifunctional catalysts *vs.* the lack of oxygen transfer in reactions with polyoxotungstates requires explanation. The important difference between polyoxomolybdates and polyoxotungstates as ligands is that the former have high oxidation potentials and reduced heteropoly blues are relatively slowly reoxidized by dioxygen whereas the latter have low oxidation potentials and are easily reoxidized by dioxygen.[7] We propose that these fundamental differences mean that the transition metal substituted polyoxomolybdates would tend to reside in a more electron rich state than the analogous polyoxotungstates thereby reducing the rate of carbon radical formation *via* electron transfer from the alkane to the polyoxometalate and therefore also reducing the rate of hydroperoxide decomposition. The decreased rate of formation and/or decomposition of intermediate hydroperoxides leads to a higher probability of oxygen transfer and formation of epoxides. Substituted transition metals in the polyoxotungstates would tend to be more electron poor thus facilitating radical formation and hydroperoxide decomposition.[8] Oxygen transfer is thereforc hardly observable. Supporting evidence for this explanation can be found by performing a reaction with a transition metal substitued polyoxovanadomolybdate *e.g.* $PCoV_2Mo_9O_{39}^{5-}$ where the polyoxometalate ligand has an even higher oxidation potential and reduced heteropoly blue is even more slowly reoxidized by dioxygen. Reaction with such a compound showed no catalytic turnovers. An alternative explanation, for the difference in polyoxomolybdate *vs.* polyoxotungstate activity could be that the former are better epoxidation catalysts than the latter, however, literature evidence[6] shows that the compounds have comparable activities in such reaction with polyoxotungstates often being the favoured catalysts.



Scheme 2

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Footnotes

† To a solution of 0.8 g (0.29 mmol) $(Bu^n_4N)_4H_3PMo_{11}O_{39}$ in 15 ml acetonitrile were added 0.0622 g (0.3 mmol) $RuCl_3{\cdot}xH_2O$ and stirred for 1 h or until all the solid was dissolved. The solvent was slowly evaporated and the resulting $(Bu^n_4N)_4PRu^{III}Mo_{11}O_{39}$ was recrystallized from a small amount of acetonitrile.

‡ At the end of the reaction the vials were cooled and the products analysed and quantified by GLC, HP5890, [15 m methylsilicone (RTX-1) 0.32 mm ID, 0.025 μm coating capillary column, He carrier gas, flame ionization detector] with authentic samples as references and cross checked by GCMS, HP 5790, identification.

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