

Polyoxometalate-catalysed epoxidation of 1-octene with hydrogen peroxide in microemulsions coupled with ultrafiltration

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Epoxidation of 1-octene with hydrogen peroxide catalysed by amphiphilic salts of peroxo tungstophosphate $\{PO_4[WO(O_2)_2]_4\}^{3-}$ in water-in-oil microemulsions is an efficient and environmentally benign reaction which, coupled with ultrafiltration, shows the potential for continuous production of epoxides.

Olefin oxides are used for manufacturing polyurethanes, unsaturated resins, surfactants and other products. The demand for them has increased over the years.¹ Polyoxometalate (POM)-catalysed epoxidation of olefins with hydrogen peroxide in biphasic systems using amphiphilic quaternary ammonium peroxo tungstophosphates as the catalyst, known as Venturullo–Ishii chemistry, is a highly efficient reaction providing high yields of epoxides under mild conditions.² Serious drawbacks of this reaction are the use of chlorinated solvents and catalyst deactivation causing difficulty in catalyst reuse.^{2e} Despite many attempts no satisfactory solutions to these problems have been found.

Microemulsions (MEs) are homogeneous, thermodynamically stable mixtures of two immiscible liquids, generally water and a nonpolar solvent, and a surfactant.³ MEs are capable of solubilising a wide spectrum of substances, e.g. a catalyst which is scarcely soluble in the reaction medium. Frequently, the rate of a reaction in an ME is higher than in conventional two-phase systems with phase transfer catalysis and even in homogeneous media because of the enrichment in reactants at the microscopic interface. ME systems are already applied in certain fields such as oil recovery, liquid–liquid extraction, pharmaceuticals and cosmetics. There is growing interest in the application of these systems for chemical and biochemical oxidation reactions.^{3,4}

We have investigated the POM-catalysed epoxidation of 1-octene with H_2O_2 in a water-in-oil (w/o) microemulsion.† The peroxo polyoxometalate $Q_3\{PO_4[WO(O_2)_2]_4\}$ (the Venturullo complex Q_3PW_4),^{2a} where Q is a quaternary ammonium cation with C_6 – C_{18} alkyl groups, was used as the catalyst. The ME system consisted of 1-octene, 27 wt% aqueous H_2O_2 and a non-ionic surfactant. The latter preferably is a biodegradable monoalkyl ether of polyethylene glycol, e.g. Brij 30® (lauryl ether of tetraethylene glycol, $C_{12}H_{25}(OCH_2CH_2)_4OH$). In this system, the olefin is simultaneously a reactant and a non-aqueous solvent for the microemulsion. A further advantage is that no co-surfactant is needed, unlike in many other cases.³ Several ionic surfactants that formed stable microemulsions such as sodium dioctyl sulfosuccinate (anionic) and cetylpyridinium chloride (cationic, with *n*-BuOH co-solvent added) were also tested but showed poor results probably because of interactions with the catalyst. Fig. 1 shows the partial phase diagram for the ternary system 1-octene–27% aqueous H_2O_2 –Brij 30 at 50 °C with w/o microemulsion on the oil-rich side. Most of our experiments refer to the composition 1-octene/27% H_2O_2 /Brij 30 = 60:10:30 (wt) marked on the phase diagram by a cross. The ME system was perfectly stable during the epoxidation. The catalyst Q_3PW_4 because of its amphiphilic nature did not affect the stability of the ME system.

In the ME system at 20–50 °C, the epoxidation occurred almost as efficiently as in the conventional biphasic

$ClCH_2CH_2Cl$ – H_2O_2 – H_2O system,^{2a,b} except no stirring was required (Fig. 2), yielding up to 95% epoxide at 100% H_2O_2 conversion in 1 h (Table 1). Only traces of 1,2-octanediol were detected. Importantly, no chlorinated solvent was used. The

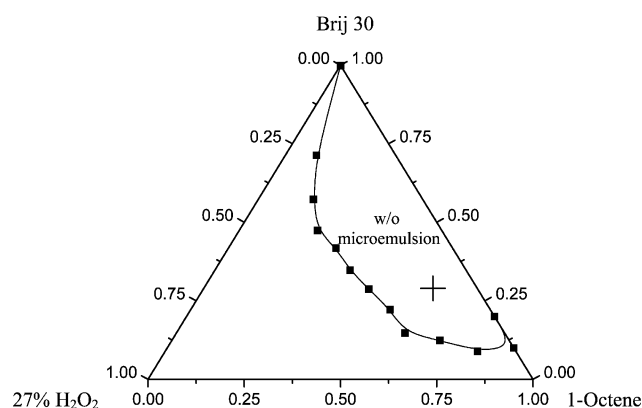


Fig. 1 Partial phase diagram for the ternary system 1-octene–27% aqueous H_2O_2 –Brij 30 at 50 °C with w/o microemulsion on the oil-rich side.

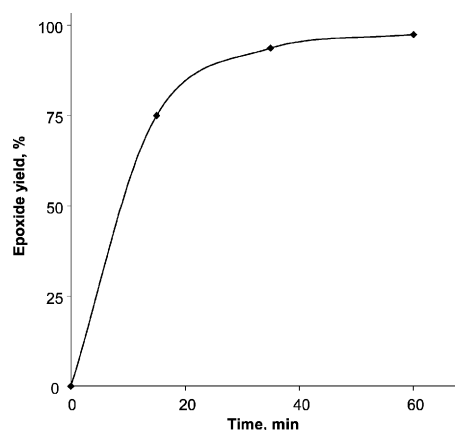


Fig. 2 Epoxidation of 1-octene catalysed by Q_3PW_4 (0.16 mmol, $Q = (n-C_8H_{17})_4N^+$) at 50 °C without stirring in the ME system containing 3.00 g (27 mmol) 1-octene, 0.50 g (4.0 mmol) 27% H_2O_2 , and 1.50 g Brij 30.

Table 1 Epoxidation of 1-octene with H_2O_2 in microemulsion catalysed by Q_3PW_4 (0.10 mmol) at 50 °C, 1 h^a

Q	TOF ^b /min ⁻¹	Epoxide yield ^c (%)
(<i>n</i> -Bu) ₄ N ⁺	—	—
CH ₃ (<i>n</i> -C ₈ H ₁₇) ₃ N ⁺	0.71	95
Aliquat 336 ^d	0.68	93
(<i>n</i> -C ₈ H ₁₇) ₄ N ⁺	1.04	95

^a ME system: 3.00 g (27 mmol) 1-octene, 0.50 g (4.0 mmol) 27% aqueous H_2O_2 and 1.50 g Brij 30. ^b Calculated from initial rates; based on 1 mol of Q_3PW_4 . ^c Based on H_2O_2 . ^d Mainly CH₃(*n*-C₈H₁₇)₃N⁺.

type of Q cation had little effect on the epoxide yield and the rate of reaction, except for (n-Bu)₄N⁺, in which case the catalyst was poorly soluble in the system. As H₂O₂ was used up in the reaction, the catalyst precipitated as a white sediment. Similar behaviour has been noted before.^{2h} Addition of fresh H₂O₂ redissolved the catalyst and restarted the reaction. This could be done several (3–4) times without breaking the ME. Hence, the ME system allows reuse *in situ* by adding more hydrogen peroxide, albeit with gradually reduced activity because of water accumulation. Our attempts to reuse the catalyst by filtering it off were unsuccessful—the isolated catalyst did not dissolve in fresh ME. Therefore, for continuous processing, water that forms in the reaction must be continuously removed from the reaction system. This was attempted using ultrafiltration.

The micellar enhanced ultrafiltration of the reaction mixture was performed using a stirred batch filtration unit with Nadir[®] membranes (4–10 kDa) under 5 bar nitrogen pressure. The ultrafiltration retained *ca.* 90% of the catalyst behind the membrane (from W analysis by ICP) and allowed removal of by-product water from the reaction system. The epoxide product could then be isolated from the filtrate, *e.g.* by distillation or other methods discussed elsewhere.³ Hence, the use of this ME system coupled with ultrafiltration shows the potential for the development of continuous POM-catalysed epoxidation of olefins with hydrogen peroxide.

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Notes and references

† *Experimental.* All chemicals were purchased from Aldrich or Fluka and used as received, except for 1-octene which was distilled prior to use. The peroxy complexes Q₃{PO₄[WO(O₂)₂]₄} were prepared according to the literature method^{2a} using Aliquat 336[®] (mainly CH₃(n-C₈H₁₇)₃NCl), CH₃(n-C₈H₁₇)₃NCl or (n-C₈H₁₇)₄NCl as a surfactant. The complexes were stored as solutions in chloroform in a stoppered glass bottle at 4 °C. The biphasic epoxidation of 1-octene was carried out as described by Venturello *et al.*^{2a} 2 ml of chloroform solution containing the catalyst, 50 mmol of octene and 1 mmol n-decane (internal standard) were added to 10 ml

dichloroethane. 25 mmol of aqueous H₂O₂ was then added and the two-phase mixture was heated to a certain temperature (50–70 °C). The reaction was monitored by GC analysis performed on a Varian CP3800 chromatograph equipped with a 30 m ZB-WAX capillary column from Zebron. In microemulsion, the epoxidation was carried out as follows. The catalyst solution in chloroform was introduced into a round-bottomed flask, and the solvent was removed under vacuum. The amount of catalyst was measured by weighing the flask after solvent removal. 1.50 g Brij[®] 30 and 3.00 g (27 mmol) 1-octene were added to the catalyst. The flask was shaken until the catalyst dissolved. The mixture was brought to a specified temperature (room temperature or 50 °C), then 0.50 g (4.0 mmol) 27 wt% aqueous H₂O₂ was added. Samples were taken at appropriate intervals and analysed by GC adding n-decane as a standard. Addition of n-decane to the reacting mixture was undesirable to avoid breaking the microemulsion. Micellar enhanced ultrafiltration of the reaction mixture was performed using a stirred batch filtration unit with Nadir[®] membranes (4–10 kDa, 45 mm diameter) under 5 bar nitrogen pressure. The membranes were kindly provided by Nadir Filtration. The phase diagram for the ternary system 1-octene–27% H₂O₂–Brij 30 was obtained at 50 °C by adding 27% H₂O₂ aqueous solution dropwise in 0.2 ml portions to 1-octene–Brij 30 mixtures of a 1:9 to 9:11 weight ratio, followed by visual inspection of the resulting system.

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