

Epoxidation of oleic acid catalyzed by peroxy phosphotungstate in a two-phase system

I.V. Kozhevnikov^{a,*}, G.P. Mulder^b, M.C. Steverink-de Zoete^b, M.G. Oostwal^b

^a *Leverhulme Centre for Innovative Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

^b *Unichema International, Buurtje 1, P.O. Box 2, 2800 AA Gouda, Netherlands*

Received 26 August 1997; accepted 22 September 1997

Abstract

The peroxy phosphotungstate $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ is a highly efficient catalyst (or catalyst precursor) for the phase-transfer epoxidation of oleic acid by aqueous 35–60% hydrogen peroxide, yielding 84% epoxide (based on oleic acid) at 95% oleic acid conversion and 800–1200 catalyst turnovers, without using a chlorocarbon solvent. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidation; Oleic acid; Polyoxometalates

1. Introduction

Tungsten and molybdenum polyoxometalates (POMs) are promising catalysts for the epoxidation of alkenes by hydrogen peroxide in two-phase systems [1–10]. Two highly effective and mechanistically closely related POM-based catalyst systems for alkene epoxidation by H_2O_2 are of particular interest, namely, those developed by the groups of Venturello and Ishii.

Venturello et al. [6–9] performed the epoxidation of alkenes in a biphasic system, e.g., $\text{CHCl}_3\text{--H}_2\text{O}$, with the use of diluted H_2O_2 (2–15%) and tungstate and phosphate ions as catalyst precursors in the presence of a phase-transfer catalyst—quaternary ammonium cation (Q^+) with $\text{C}_6\text{--C}_{18}$ alkyl groups. In this system, a peroxy POM, $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, analogous to the molybdenum peroxy POM first reported by Beiles et al. [10], was isolated and characterized [6]. The anion $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ has the C_2 symmetry and consists of the central PO_4 tetrahedron linked through its oxygen atoms to two pairs of edge-sharing distorted pentagonal bipyramids $\text{W}(\text{O}_2)_2\text{O}_3$. Each tungsten atom is linked to two peroxy groups—one non-bridging (η^2) and the other bridging (η^2, η^1)—located in the equatorial plane of the pentagonal bipyramid. This peroxy complex was found to be remarkably effective in

* Corresponding author. Fax: +44-151-7943589; e-mail: kozhev@liverpool.ac.uk

stoichiometric as well as in catalytic biphasic oxidation of alkenes by H_2O_2 and was postulated to be the active oxygen transfer agent in alkene epoxidation.

Ishii et al. [11–13] demonstrated that the epoxidation of alkenes as well as oxidation of a variety of organic substrates with 35% H_2O_2 can be effectively performed in a homogeneous phase or biphasic system with the use of cetylpyridinium salt of the Keggin-type heteropoly acid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ as a catalyst precursor, with the cetylpyridinium cations providing the phase-transfer function. The two-phase epoxidation of alkenes by hydrogen peroxide in the presence of $\text{PW}_{12}\text{O}_{40}^{3-}$ was suggested to proceed through the formation of an active peroxo POM in the aqueous phase by interacting the Keggin heteropolyanion with hydrogen peroxide. With the phase-transfer catalyst, Q^+ , the peroxo POM is almost fully transferred into the organic phase. The reaction takes place preferentially in the organic phase via the oxygen atom transfer from the peroxo POM to the substrate. The peroxo POM is then regenerated at the interface by interacting with H_2O_2 [11].

In recent years, the Venturello–Ishii chemistry has been investigated by several groups [14–21]. It has been shown that the epoxidation of alkenes in the Venturello system and in the Ishii system, despite the use of different catalyst precursors, includes nearly identical peroxo polyoxometalate intermediates [14–18]. Thus, several peroxo polyoxometalates of the composition $\text{PW}_x\text{O}_y^{z-}$ ($x = 1–4$), related to the Venturello peroxo anion $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, have been found [17]. These may be the active species or catalyst precursors in the phase-transfer olefin epoxidation. Evidence has been provided that $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ is the active species in the olefin epoxidation [21]. Catalyst deactivation as well as the use of chlorinated hydrocarbons as solvents have been mentioned as the major drawback to the Venturello–Ishii epoxidation [21].

In the present work we report on the epoxidation of oleic acid by the Venturello–Ishii system, which is of interest as a step for the production of a series of oleochemical-based polymers derived from renewable natural resources [22,23].

2. Experimental

2.1. Materials

Aqueous hydrogen peroxide (35 and 60 wt.%) was obtained from Interlox. High Oleic Sunflower Acid from Unichema, containing (wt.%) oleic acid (76), linoleic acid (7), palmitic acid (5), stearic acid (6), erucic acid (1), and high molecular weight components (esters) (5), was used as a source of oleic acid. A few experiments were carried out with 99% oleic acid (from Aldrich); the results were similar to those with High Oleic Sunflower Acid.

The peroxo phosphotungstate $\text{Q}_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$ (**I**) was prepared by the literature method [6–9], using Aliquat 336 $[\text{CH}_3(n\text{-C}_8\text{H}_{17})_3\text{NCl}]$ as a surfactant. A 0.05 mol l^{-1} stock solution of **I** in CH_2Cl_2 was used as catalyst in all experiments. The catalyst solution was stored in a stoppered glass bottle at 4°C . Under such conditions, it was fairly stable; no loss of catalytic activity was observed over a period of at least 2 months.

2.2. NMR spectroscopy

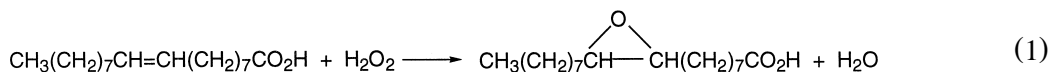
A 121.5 MHz ^{31}P NMR solution spectra were taken on a Varian VXR-400S spectrometer. One percent H_3PO_4 in D_2O was used as an external reference.

2.3. Epoxidation

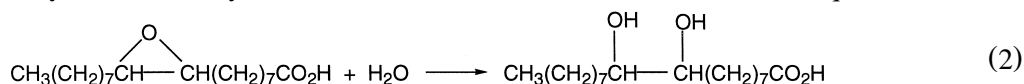
The epoxidation of oleic acid (OA) by aqueous H_2O_2 was carried out under air at 50–80°C in a two-phase system, OA-aqueous H_2O_2 , without any solvent added. The reaction was performed in a 75 ml double-walled glass vessel equipped with a magnetic stirrer. Typically, the reactor was charged with 10 g (0.03 mol) of OA feed. The stirred system was heated to the reaction temperature. Then the 0.05 mol l^{-1} catalyst stock solution in CH_2Cl_2 (0.5–0.75 ml, 0.025–0.038 mmol **I**) was added. The reaction was started by adding H_2O_2 (0.035–0.05 mol) to the stirred mixture. A total of 35% H_2O_2 was added all at once. With 60% H_2O_2 the reaction was almost immediately exothermic; in this case H_2O_2 was added dropwise over a period of 5 to 20 min. Periodically, 0.02 ml aliquots were taken, esterified with a diethyl ether solution of diazomethane and analyzed by GC (Varian Star 3400 CX, CP Sil 5 CB 25 m \times 0.25 mm column, FID, the temperature range of 50–320°C/10°C min^{-1}). Products were identified by GC, using authentic samples provided by Unichema Int. High molecular weight components (HMW) were analyzed by gel permeation chromatography (GPC), using a HPLC set-up with a refraction index detector and three 30 cm \times 7 mm GPC columns (PL gel, 5 μm polymer beads) with pore sizes of 100, 500 and 1000 Å. The GPC analysis was performed at 40°C, using tetrahydrofuran as a mobile phase.

3. Results and discussion

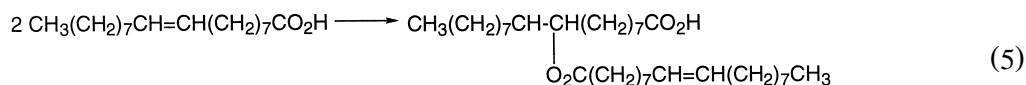
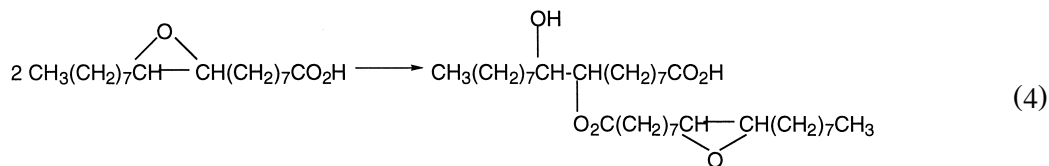
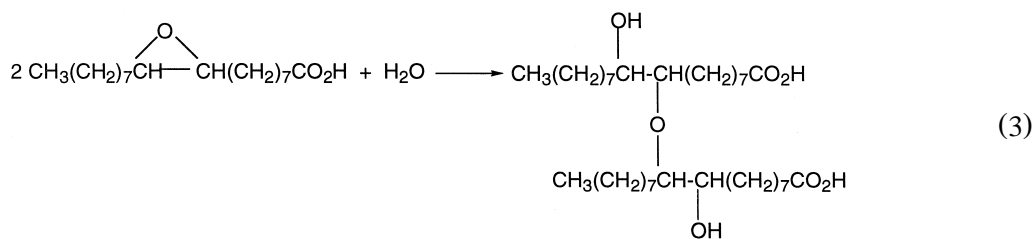
Unsaturated fatty acids derived from renewable natural resources provide a unique substrate for the production of commercially important monomers for various condensation polymers, stabilizers, automobile lubricating oil formulations, etc., [22,23]. Epoxidation of oleic acid (Eq. (1)) is interesting for the synthesis of specialty polymers and polyesters for synthetic lubricants [22,23]. A closely relevant reaction, the hydroxylation of OA by hydrogen



peroxide catalyzed by tungstic acid, H_2WO_4 , yielding a diol, 9,10-dihydroxystearic acid (DHSA), proceeds through the intermediate formation of OA epoxide [24]. Generally, the hydroxylation of OA is performed at 55–80°C in a two-phase substrate-aqueous H_2O_2 system with 60–70 wt.% H_2O_2 (1.5–2 fold molar excess over OA) and 0.3–2 wt.% H_2WO_4 based on OA. In this system, the aqueous phase is strongly acidic (pH 0–1); the acidity is generated by the interaction between H_2WO_4 and H_2O_2 , forming active peroxo complexes of W(VI). Under such conditions, the initially formed oleic acid epoxide hydrolyzes in situ to yield 60–80% *trans*-9,10-DHSA based on OA (Eq. (2)) [24].



The drawback of this reaction is that ca. 20% of a high molecular weight byproduct (HMW) is formed. This may be due to the acid-catalyzed reactions represented by Eqs. (3)–(5). Free radical oligomerization of OA induced by the decomposition of H_2O_2 may be envisaged, too. To overcome this drawback, a more efficient catalyst is required allowing the epoxidation of OA in a less acidic system and at a lower temperature.



Here we report on the epoxidation of OA by the Venturello–Ishii system, which has been found to be superior to tungstic acid in this reaction. Representative results are given in Table 1. The epoxidation of OA by H_2O_2 catalyzed by **I** proceeds readily at 50–80°C reaching 94–99% OA conversion in 0.5–1.7 h. This system is much less acidic than $\text{H}_2\text{WO}_4/\text{H}_2\text{O}_2$: the aqueous phase has

Table 1
Epoxidation of oleic acid by aqueous H_2O_2 catalyzed by $\text{Q}_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{\text{a}}$

Entry	Catalyst mmol (%)	$\text{H}_2\text{O}_2^{\text{b}}$ mol (%)	T (°C)	Time (min)	Conversion ^c (%)	Selectivity (%) ^d		HMW (wt.%)
						Epoxide	Diol	
1	0.12 ^e	0.050 (60)	80	160	93	Trace	66	20
2	0.12 ^{e,f}	0.050 (60)	80	270	30	37	3.2	— ^g
3	0.025	0.050 (35)	80	60	95	62	4.1	23.8
4	0.025 ^h	0.050 (35)	80	60	47	19	24	— ^g
5	0.038	0.050 (35)	80	50	99	57	5.7	25.8
6	0.038 ⁱ	0.050 (60)	60	30	98	80	3.1	9.3
7	0.038	0.050 (35)	60	105	99	75	1.7	15.7
8	0.038 ⁱ	0.050 (60)	60	70	99	54	4.9	15.8
9	0.038 ^j	0.041 (60)	60	35	98	77	6.4	9.5
10	0.038 ^j	0.041 (60)	60	50	95	89	1.3	5.0
11	0.038 ^j	0.035 (60)	50	45	94	88	1.3	6.4

^aIn all cases, 10 g (0.03 mol) of the OA feed, containing 76% OA, 7% linoleic acid, 5% palmitic acid, 6% stearic acid, 1% erucic acid, and 5% HMW, was charged.

^bIn parentheses the concentration of the initial aqueous H_2O_2 (35 or 60 wt.%).

^cTotal conversion of oleic and linoleic acids.

^dTotal selectivity to epoxides and diols derived from oleic and linoleic acids (based on unsaturated fatty acids).

^e H_2WO_4 catalyst; 60% H_2O_2 added dropwise during 75 min.

^f0.8 mmol of NaHCO_3 added; the aqueous phase had pH 3–4.

^gHMW not measured.

^h0.6 mmol of 96% H_2SO_4 added; the aqueous phase had pH 1–2.

ⁱ60% H_2O_2 added dropwise during 5 min.

^j60% H_2O_2 added dropwise during 20 min.

pH 3–4. As a result, OA epoxide is the major product (54–89% selectivity), with a small amount of diol DHSA (1.3–5.7%) also being formed. Addition of sulfuric acid to the aqueous phase, lowering the pH to 1–2, slowed the reaction and increased the selectivity to diol at the expense of epoxide, as expected (Entry 4). Use of 60% H_2O_2 gives the best results, yielding 84% epoxide (based on OA) at 60°C (Entry 10). However, the reaction with 35% H_2O_2 is also quite efficient. A relatively small excess of H_2O_2 (20–40% mol) over OA is required to complete the reaction. The efficiency of the catalyst is very high: 800–1200 catalyst turnovers are readily achieved.

Typically, in the Venturello–Ishii epoxidation a chlorocarbon solvent (CCl_4 , CHCl_3 , CH_2Cl_2 , etc.) is used [6–10], which is the major drawback of this method [21]. The few examples of the reaction in different solvents reported so far [11] are relatively inefficient. Advantageously, the OA epoxidation by the Venturello–Ishii system is very efficient without any solvent. Apparently, the solubility of **I** in OA is sufficient to run the reaction. Although, for convenience, we use a concentrated solution of **I** in CH_2Cl_2 as a catalyst stock, **I** can be handled as a solid as well.

The last column of Table 1 shows the amount of high molecular weight components (HMW) formed in the reaction system. As seen, the yield of HMW depends mainly on the temperature and the reaction length. At 80°C the HMW content is quite high, 24–26 wt.% (Entries 3, 5). But under optimum conditions at 50–60°C, it drops down to 5–6 wt.% (Entries 10, 11). Given the HMW amount of 5 wt.% in the OA feed, practically no HMW is formed under such conditions.

For comparison, Table 1 shows results for the reaction in $\text{H}_2\text{WO}_4/\text{H}_2\text{O}_2$ system (Entry 1). In this system (pH 0–1), with 60% H_2O_2 at 80°C, the diol is obtained as the major product with 66% selectivity at 93% conversion together with 20% HMW. With 35% H_2O_2 under otherwise the same conditions, the reaction is very slow. In a less acidic system (pH 3–4 adjusted by NaHCO_3), the reaction slowed down; the epoxide became the major product, as expected (Entry 2). It is seen that the **I**/ H_2O_2 system is more active than $\text{H}_2\text{WO}_4/\text{H}_2\text{O}_2$, both per mole of the catalyst and per tungsten atom, in converting OA into oxygenated products, epoxide or diol, respectively. Particularly important is that the **I**/ H_2O_2 system allows the formation of HMW to be practically completely eliminated.

Although mechanistic considerations are beyond the scope of this work, some pertinent points can be mentioned. Apparently, the **I**/ H_2O_2 system is quite a complex one [16–18]. Fig. 1 shows the ^{31}P NMR spectrum of the stock solution of **I** in CH_2Cl_2 . The spectrum is similar to the one for an ‘aged’ solution of **I** in CHCl_3 reported earlier [21] and contains the line at 1.9 ppm assigned to $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ [21] and three other unidentified signals at –8.7, –6.8 and 7.3 ppm probably from peroxo polyanions $\text{PW}_x\text{O}_y^{z-}$ ($x = 1-4$), containing diperoxo units $\text{WO}(\text{O}_2)_2$ [17]. Reportedly, the aged solution of **I** in CHCl_3 showed much lower catalytic activity than the fresh solution in the epoxidation of 1-octene by H_2O_2 in a two-phase system $\text{CHCl}_3\text{--H}_2\text{O}$ [21]. On this and other bases, $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ was suggested to be the only active species in the olefin epoxidation by the

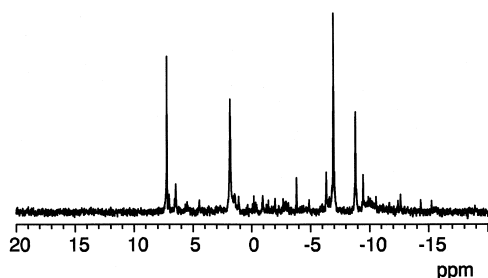


Fig. 1. The 121.5 MHz ^{31}P NMR spectrum of 0.05 mol l^{-1} solution of **I** in CH_2Cl_2 .

Venturello–Ishii system [21]. In contrast, in our case the aged solution of **I** in CH_2Cl_2 efficiently catalyzes the epoxidation of OA. The stock solution of **I** in CH_2Cl_2 stored for at least 2 months did not lose its activity at all. Recently, it has been shown that the units $\text{WO}(\text{O}_2)_2$ in the peroxo polyanions $\text{PW}_x\text{O}_y^{z-}$ are quite labile [18], hence the different peroxo phosphotungstic species present in the system are likely to exist in a fast equilibrium. This is suggestive that besides $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$ other peroxo POMs existing in the system may play an active role in the epoxidation.

Acknowledgements

This research was supported by Unichema International. The authors are grateful to Prof. Herman van Bekkum for his interest and valuable discussions and to Dr. Joop Peters for measuring the NMR spectra.

References

- [1] C.L. Hill, C.M. Prosser-McCartha, *Coord. Chem. Rev.* 143 (1995) 407.
- [2] N. Mizuno, M. Misono, *J. Mol. Catal.* 64 (1990) 1.
- [3] N.L. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov, V.A. Likholobov, *Kinet. Katal.* 33 (1992) 516.
- [4] M. Schwegler, M. Floor, H. van Bekkum, *Tetrahedron Lett.* 29 (1988) 823.
- [5] H. Furukawa, T. Nakamura, H. Inagaki, E. Nishikawa, C. Imai, M. Misono, *Chem. Lett.*, 1988, p. 877.
- [6] C. Venturello, R. D'Aloisio, J.C.J. Bart, M. Ricci, *J. Mol. Catal.* 32 (1985) 107.
- [7] C. Venturello, E. Alneri, M. Ricci, *J. Org. Chem.* 48 (1983) 3831.
- [8] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1988) 1553.
- [9] C. Venturello, M. Gambaro, *Synthesis*, 1989, p. 295.
- [10] R.G. Beiles, Z.E. Rozmanova, O.B. Andreeva, *Russ. J. Inorg. Chem.* 14 (1969) 1122.
- [11] Y. Ishii, M. Ogawa, in: A. Ohno, N. Furukawa (Eds.), *Reviews on Heteroatom Chemistry*, Vol. 3, MYU, Tokyo, 1990, p. 121.
- [12] Y. Matoba, H. Inoue, J. Akagi, T. Okabayashi, Y. Ishii, M. Ogawa, *Synth. Commun.* 14 (1984) 865.
- [13] S. Sakaguchi, S. Watase, Y. Katayama, Y. Sakata, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* 59 (1994) 5681.
- [14] L.J. Csanyi, K. Jaky, *J. Mol. Catal.* 61 (1990) 75.
- [15] L.J. Csanyi, K. Jaky, *J. Catal.* 127 (1991) 42.
- [16] C. Aubry, G. Chottard, N. Platzler, J.M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, *Inorg. Chem.* 30 (1991) 4409.
- [17] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.M. Brégeault, *Inorg. Chem.* 33 (1994) 871.
- [18] L. Salles, J.Y. Piquemal, R. Thouvenot, C. Minot, J.M. Brégeault, *J. Mol. Catal. A* 117 (1996) 375.
- [19] N.M. Gresley, W.P. Griffith, A.C. Laemmel, H.I.C. Nogueira, B.C. Parkin, *J. Mol. Catal. A* 117 (1997) 185.
- [20] F.P. Ballistreri, A. Bazzo, G.A. Tomaselli, R.M. Toscano, *J. Org. Chem.* 57 (1992) 7074.
- [21] D.C. Duncan, R.C. Chambers, E. Hecht, C.L. Hill, *J. Am. Chem. Soc.* 117 (1995) 681.
- [22] R.G. Fayer, in: H. Eierdanz (Ed.), *Perspektiven nachwachsender Rohstoffe in der Chemie*, VCH, Weinheim, 1996, pp. 107–117.
- [23] H.A. Wittcoff, B.G. Reuben, *Industrial Organic Chemicals*, Wiley, New York, 1996.
- [24] T.M. Luong, H. Schriftman, D. Swern, *J. Am. Oil Chem. Soc.* 44 (1967) 316.