Catalysis Communications 26 (2012) 93–97

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Oxidations by the system 'hydrogen peroxide–$[Mn_2L_2O_3]^{2+}$ ($L=1,4,7$-trimethyl-1,4,7-triazacyclononane)–carboxylic acid' Part 13. Epoxidation of methyl oleate in acetonitrile solution [1]

Dalmo Mandelli [a,*], Yuriy N. Kozlov [b], Wagner A. Carvalho [a], Georgiy B. Shul'pin [b,**]

[a] Center of Natural and Human Sciences, Federal University of ABC (UFABC), Santa Adélia Street, 166, Bangu, Santo André, SP, 09210-170, Brazil
[b] Semenov Institute of Chemical Physics, Russian Academy of Sciences, Ulitsa Kosygina, dom 4, Moscow 119991, Russia

ARTICLE INFO

Article history:
Received 22 February 2012
Received in revised form 3 April 2012
Accepted 12 April 2012
Available online 25 April 2012

Keywords:
Biodiesel
Epoxidation
Fatty acid methyl esters (FAMEs)
Homogeneous catalysis
Manganese complexes
Renewables

ABSTRACT

Methyl oleate can be efficiently (yield and selectivity attain 100%, turnover number is up to 2000) epoxidized with hydrogen peroxide in acetonitrile solution at 25 °C using the combination "$[Mn_2L_2O_3](PF_6)_2$ ($L=1,4,7$-trimethyl-1,4,7-triazacyclononane)/oxalic acid" as a catalyst. Kinetic features of the reaction were studied and the conclusion has been made that high-valent oxo-manganese rather than hydroxyl radicals is a crucial oxidizing species in this process.

1. Introduction

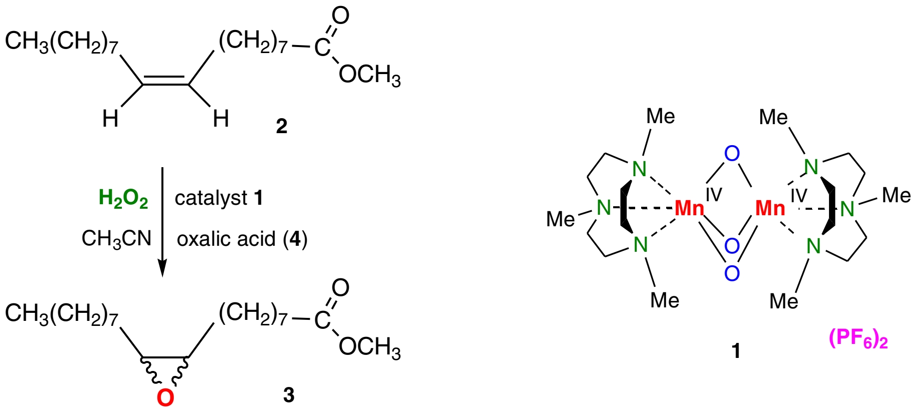
Modified vegetable oils play an important role in the modern chemical industry because they can be easily obtained from renewable resources [2–4]. Unsaturated vegetable oils (for example, soybean oil contains 23% oleic acid) can be epoxidized [5–7] to various products that are used as building blocks for the preparation of valuable chemical intermediates: reactive diluents for paints and intermediates in the production of polyurethane-polyols. Epoxides of fatty acid methyl esters (FAMEs) play an important role as intermediates in the production of lubricants, plasticizers in polymers and stabilizers in chlorine-containing resins, and they find applications in the manufacture of cosmetics, wood impregnation, pharmaceuticals, and bio-fuel additives. Methyl oleate [methyl (Z)-octadec-9-enoate; a component of the Queen Retinue Pheromone [8]; compound **2** in Scheme 1] and methyl epoxystearate (the epoxide obtained from methyl oleate epoxidation; compound **3** in Scheme 1) are among such practically valuable substances. Catalytic oxygenation of methyl oleate with hydrogen peroxide is one of the promising routes to the important epoxide.

The dinuclear manganese(IV) complex $[LMn(O)_3MnL](PF_6)_2$ (catalyst **1**; L is 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN; see Scheme 1) as well as some similar compounds [9–11] are known to catalyze oxidations of olefins and phenols. Earlier some of us discovered that compound **1** catalyzes the oxidation of various organic compounds by hydrogen peroxide much more efficiently if a small amount of a carboxylic acid is added to the reaction solution [1,12–28]. The '**1**/carboxylic acid/H_2O_2' system in acetonitrile solution very efficiently epoxidizes olefins [14,16–18,24], transforms alcohols into ketones (aldehydes) [14,19,23], sulfides into sulfoxides [14] and causes the degradation of dye Rhodamine 6G [22]. The reaction with olefins gave rise to the products of dihydroxylation [16] in addition to the corresponding epoxides. The combination '**1**/carboxylic acid/H_2O_2' oxidizes also inert alkanes in acetonitrile [12–16,20,21] to afford primarily the corresponding alkyl hydroperoxides which are transformed further into the more stable ketones (aldehydes) and alcohols. Olefins [17], alcohols [19] and alkanes [17] were oxidized also in the absence of acetonitrile. Olefins and alkanes can be oxidized by *tert*-butyl hydroperoxide [14] or peroxyacetic acid [12,25] using complex **1** as a catalyst. The reaction with *tert*-butyl hydroperoxide is significantly accelerated in the presence of a small

---

* Corresponding author.
** Corresponding author. Fax: +7 499 1376130.
E-mail addresses: dalmo.mandelli@uol.com.br (D. Mandelli), Shulpin@chph.ras.ru (G.B. Shul'pin).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2012.04.019



Scheme 1. Epoxidation of methyl oleate (**2**) catalyzed by complex **1**.

amount of a carboxylic acid [14]. Very recently, it was reported that, similar to our system, alkene epoxidation with H_2O_2 catalyzed by the manganese(V) nitrido complex $(PPh_4)_2[Mn(N)(CN)_4]$ is greatly enhanced by the presence of just one equivalent of acetic acid [29].

In the present work we report first results on the epoxidation of methyl oleate (compound **2**) to the corresponding epoxide (compound **3**) with H_2O_2 in acetonitrile catalyzed by complex **1** and oxalic acid (compound **4**; see Scheme 1). Oxalic acid is an obligatory component of the catalytic system.

2. Results and discussion

We have found that methyl oleate (**2**) can be easily epoxidized to **3** with aqueous H_2O_2 in acetonitrile solution under very mild conditions if complex **1** and a small amount of oxalic acid (**4**) are present. Examples of the kinetic curves of the reactions carried out under different conditions are presented in Fig. 1. When a very low concentration of catalyst **1** is used and the $[H_2O_2]_0/[2]_0$ ratio is 2 the initial rate of the reaction is relatively low and final yield of **3** attains only 63% (Fig. 1A). However, at higher concentration of **1** (5×10^{-5} M) and $[H_2O_2]_0/[\mathbf{2}]_0=5$ maximum yield 100% is achieved after only 2 h (Fig. 1B). Turnover number (TON, moles of **3** per 1 mol of **1**) is 2000. Since a large excess of H_2O_2 is used in this case some over-oxidation occurs and after 10 h yield of **3** is lower in comparison with that obtained after 2 h. The optimal conditions for the epoxidation were found at $[\mathbf{1}]_0=5\times10^{-5}$ M and $[H_2O_2]_0/[\mathbf{2}]_0=2.25$ (Fig. 1C). In this case maximum yield 100% and TON = 2000 were attained after 10 h. The selectivity is close to 100%.

Fig. 2 demonstrates that the initial epoxidation rate is proportional to the initial concentration of **1** in the interval $0\div5\times10^{-5}$ M. It can be seen in Fig. 3A that the initial rate W_0 does not depend on the concentration of oxalic acid (**4**) in the interval of its concentration $[\mathbf{4}]=0.002\div0.012$ M. It is reasonable to assume that the accelerating effect of the oxalic acid additives is due to the formation of an *adduct* between complex **1** and oxalic acid:

$$\mathbf{1}+\mathbf{4}\rightleftarrows adduct \quad \text{equilibrium constant } K_1.$$

Taking into account the fact that there is no effect of **4** additive up to its concentration $[\mathbf{4}]=0.002$ M allows us to estimate the low limit for the equilibrium constant:

$$K_1[\mathbf{4}]\gg1.$$

Consequently, $K_1\gg500\ M^{-1}$. Yields of **3** after 2 and 10 h (Fig. 1B and C, respectively) only slightly depend on concentration of added oxalic acid.

The initial epoxidation rate does not depend on the initial concentration of substrate **2** in the interval of its concentrations $[\mathbf{2}]_0=0.03\div0.12$ M (Fig. 4A). These data allow us to propose the epoxidation mechanism which does not involve hydroxyl radicals as oxidizing species. Indeed, if hydroxyl radicals are involved into the process, the competitive interaction of these radicals with **2** and acetonitrile should give the half of the maximum epoxidation rate at

$$\frac{k_{MeCN}[MeCN]}{k_2[2]}\approx1.$$

However, it is known that the half-effect for the cyclohexane oxidation with the participation of hydroxyl radicals can be measured at cyclohexane concentration close to 0.2 M [30]. The rate constant for the interaction between hydroxyl radicals and **2** should be only a few times higher than the corresponding constant for the reaction with cyclohexane. Due to this the half-effect should be attained at $[\mathbf{2}]_0>0.02$ M. In contrast, the experimental data presented in Fig. 4A demonstrate that this effect is attained at the **2** concentration which is much lower than 0.02 M. This conclusion is in a good agreement with our previous proposal [22,25]. The oxidations catalyzed by manganese complexes are believed to proceed with the participation of a high-valent oxo-manganese species [31–35]. Fig. 1 demonstrates that the reaction proceeds with pronounced auto-acceleration. This shape of the kinetic curves testifies that in the initial period of the reaction a catalytically active species is generated. This species is apparently a high-valent oxo-manganese derivative. As it can be expected, absolute concentrations of **3** (in M) obtained after 2 and 10 h depend on the initial concentration of **2** (Fig. 4B and C, respectively).

The linear dependence of the initial epoxidation rate on the initial H_2O_2 concentration was found when concentration of water was maintained fixed (Fig. 5A). Yield of **3** after 2 h is proportional to $[H_2O_2]_0$ (Fig. 5B) and the reaction during 10 h leads to maximum yield ($0.08\div0.10$ M) for the interval $[H_2O_2]_0=0.15\div0.25$ M (Fig. 5C). Addition of some water does not dramatically affect the initial rate (Fig. 6).

We also explored the effect of other acids as co-catalysts in the epoxidation of methyl linoleate. The results are summarized in Table 1. It can be seen that oxalic acid is the best co-catalyst for this process.

3. Conclusions

Here we describe a very efficient and green method for the epoxidation of methyl oleate with aqueous H_2O_2 in acetonitrile catalyzed by a manganese complex in obligatory combination with oxalic acid.

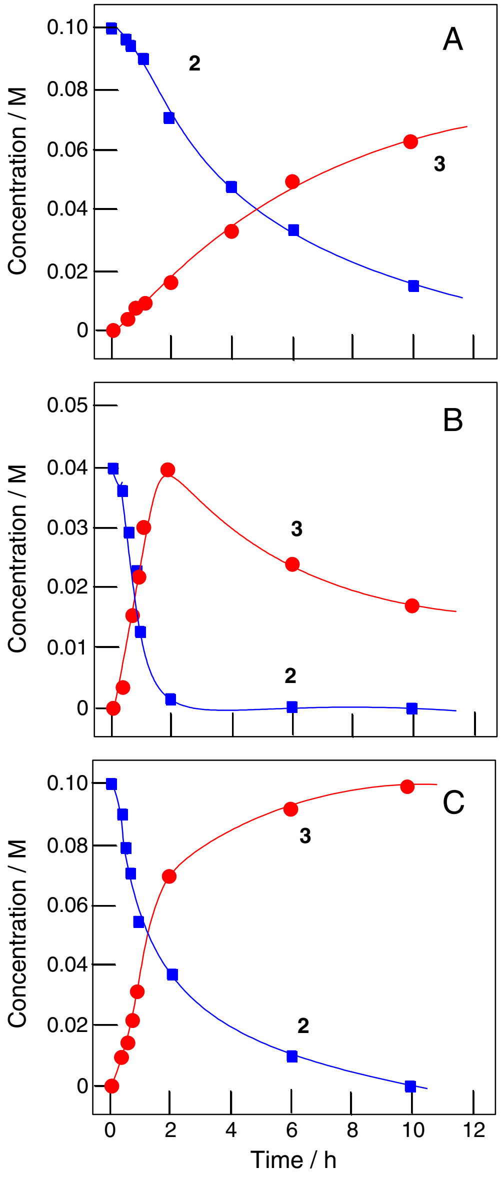


Fig. 1. Consumption of methyl oleate (curve **2**) and accumulation of methyl oleate epoxide (curve **3**) in the oxidation of methyl oleate (compound **2**) with H_2O_2 catalyzed by complex **1** in the presence of oxalic acid (compound **4**) at 25 °C in acetonitrile at different concentrations of the reactants. Graph A: $[\mathbf{2}]_0 = 0.1$ M; $[\mathbf{1}]_0 = 2\times10^{-5}$ M; $[\mathbf{4}]_0 = 0.01$ M; $[H_2O_2]_0 = 0.2$ M; yield of **3** based on **2** was 63% after 10 h; TON = 1260. Graph B: $[\mathbf{2}]_0 = 0.04$ M; $[\mathbf{1}]_0 = 5\times10^{-5}$ M; $[\mathbf{4}]_0 = 0.01$ M; $[H_2O_2]_0 = 0.2$ M; yield of **3** based on **2** was 100% after 2 h; TON = 2000. Graph C: $[\mathbf{2}]_0 = 0.1$ M; $[\mathbf{1}]_0 = 5\times10^{-5}$ M; $[\mathbf{4}]_0 = 0.0125$ M; $[H_2O_2]_0 = 0.225$ M; yield of **3** based on **2** was 100% after 10 h; TON = 2000.

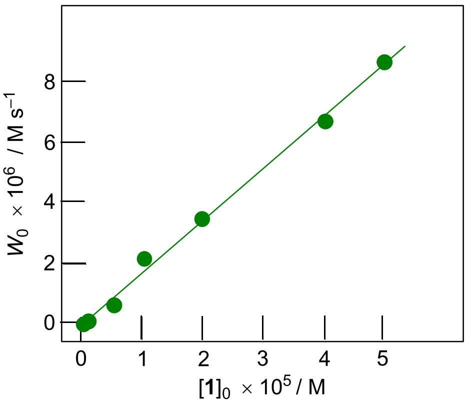


Fig. 2. Dependence of the initial reaction rate W_0 in the epoxidation of methyl oleate (**2**; initial concentration 0.1 M) with H_2O_2 (0.2 M) catalyzed by complex **1** in the presence of **4** (0.01 M) on initial concentration of **1**. Reaction was at 25 °C in acetonitrile.

4. Experimental

The catalyst was prepared as described in [15]. The oxidations of hydrocarbons in acetonitrile were carried out in air in thermostated vessels under vigorous stirring. Typically, the reaction started by the addition of an oxidant to the mixture containing catalyst, co-catalyst, substrate ("Aldrich") and solvent. The total volume of the reaction mixture was 5 mL, and 70% aqueous H_2O_2 ("Peróxidos do Brasil") was used as the oxidant. CAUTION: the combination of air and H_2O_2 with organic compounds at elevated temperatures may be explosive! Samples of the reaction mixture were analyzed by GC (Agilent 6890, N_2 was carrier gas, FID) and GC–MS (Shimadzu QP-2010 Plus, He was carrier gas); in both instruments the column was BP-20 (SGE; polyethyleneglycol — 30 m × 250 μm × 0.25 μm). Attribution of peaks was made by comparison with chromatograms of authentic samples and by GC–MS. In the kinetic study of the alkane

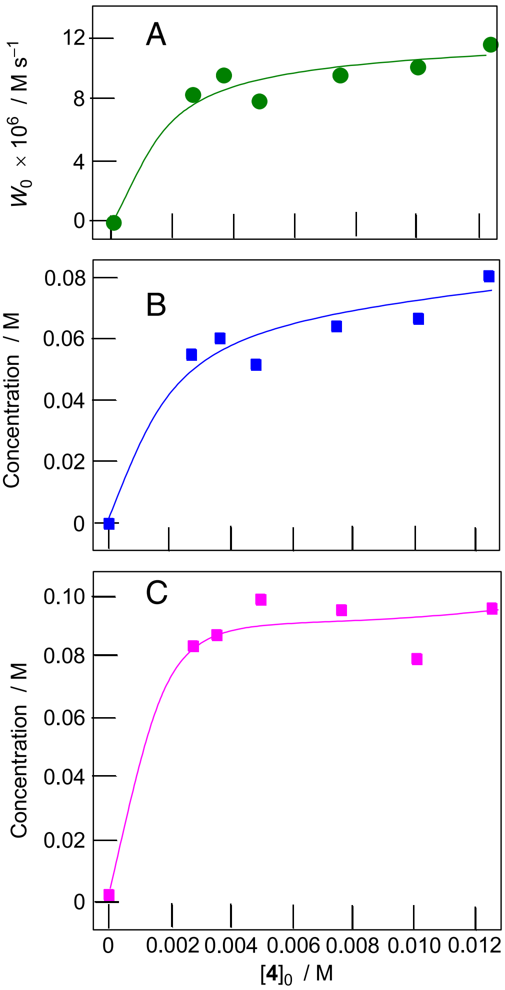


Fig. 3. Dependence of the initial reaction rate (Graph A) and concentration of **3** after 2 h (Graph B) and 10 h (Graph C) in the epoxidation of methyl oleate (**2**; initial concentration 0.1 M) with H_2O_2 (0.2 M) catalyzed by complex **1** (5×10^{-5} M) in the presence of **4** on initial concentration of **4**. Reaction was at 25 °C in acetonitrile.

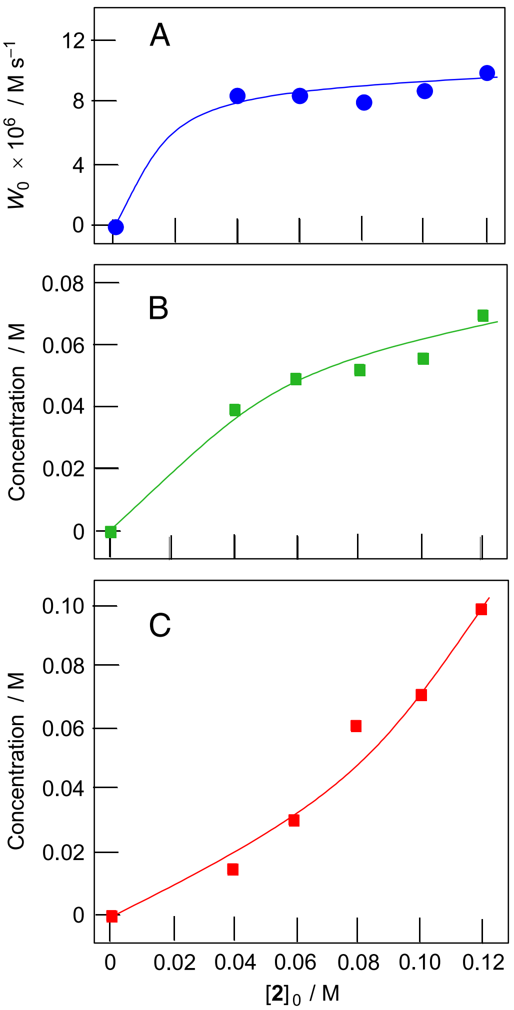


Fig. 4. Dependence of the initial reaction rate (Graph A) and concentration of **3** after 2 h (Graph B) and 10 h (Graph C) in the epoxidation of methyl oleate (**2**) with H_2O_2 (0.2 M) catalyzed by complex **1** (5×10^{-5} M) in the presence of **4** (0.01 M) on initial concentration of **2**. Reaction was at 25 °C in acetonitrile.

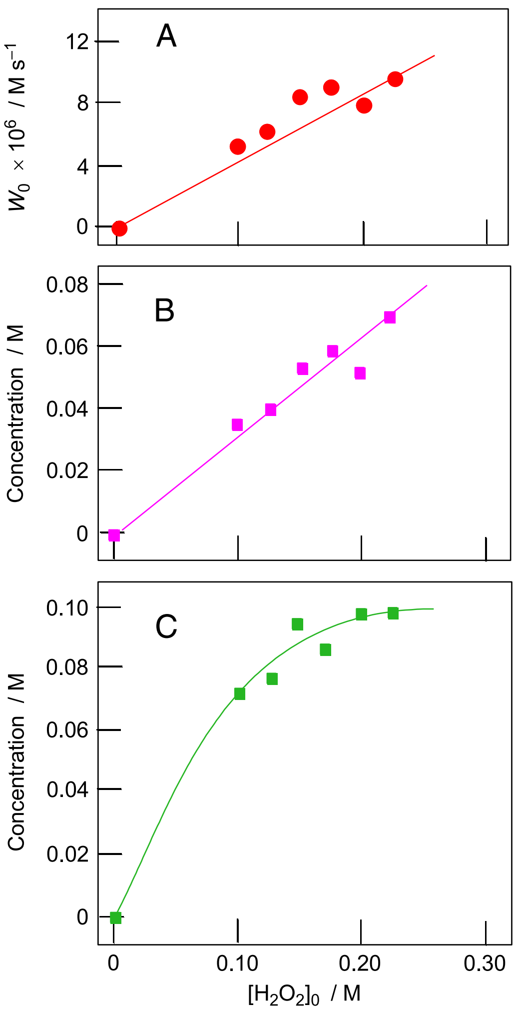


Fig. 5. Dependence of the initial reaction rate (Graph A) and concentration of **3** after 2 h (Graph B) and 10 h (Graph C) in the epoxidation of methyl oleate (**2**, initial concentration 0.10 M) with H_2O_2 catalyzed by complex **1** (5×10^{-5} M) in the presence of **4** (0.01 M) on initial concentration of H_2O_2. Concentration of H_2O was maintained constant (0.165 M) in all runs. Reaction was at 25 °C in acetonitrile.

oxidation, we measured the concentrations of **2** and **3** after the treatment with PPh_3 because in this case H_2O_2 and all peroxides present in the solution are reduced and additional oxidative processes do not proceed in the chromatograph. Hence, this method gives the most precise values of total concentrations of the substrate and product.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grant No. 12-03-00084-a), the State of São Paulo Research Foundation (Fundação de Amparo a Pesquisa do Estado de São Paulo, FAPESP; grant nos. 2005/51579-2, 2006/03996-6), the Brazilian National Council on Scientific and Technological Development (Conselho Nacional de Desenvolvimento Cientifico e Tecnológico, CNPq, Brazil; grant nos. 300984/2004-9, 478165/2006-4, 305014/2007-2), and the Fundação para a Ciência e a Tecnologia (FCT), Portugal (project PTDC/QUI-QUI/119561/2010). The authors thank Miss Danielle C. Silva for her participation in the experiments. G.B. Shul'pin expresses his gratitude to the FAPESP (grant No. 2006/03984-8) and the CNPq (grant No. 300601/01-8) for the financial support.

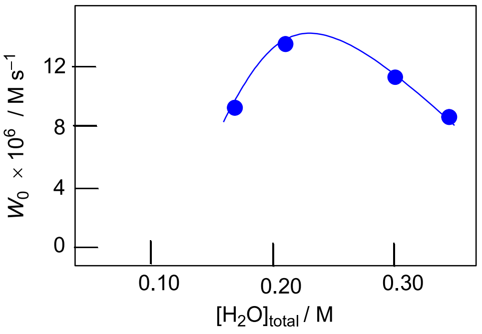


Fig. 6. Dependence of the initial reaction rate in the epoxidation of methyl oleate (**2**, initial concentration 0.10 M) with H_2O_2 (0.2 M) catalyzed by complex **1** (5×10^{-5} M) in the presence of **4** (0.01 M) on the total concentration of H_2O present in the solution. Reaction was at 25 °C in acetonitrile.

Table 1
Epoxidation of methyl oleate (**2**) to the epoxide **3** co-catalyzed by various acids.[a]

Acid	Concentration (M)	Yield of **3** (% based on **2**) after		
		1 h	2 h	10 h
None	–	0	0	1
Oxalic (**4**)	0.012	43	83	100
Acetic	0.010	0	0	2
Trifluoroacetic	0.010	58	65	70
Nitric	0.010	2	3	7

[a] Conditions. $[\mathbf{2}]_0 = 0.1$ M; $[\mathbf{1}]_0 = 5 \times 10^{-5}$ M; $[H_2O_2]_0 = 0.21$ M; 25 °C; in acetonitrile.

References

[1] For a review, see: G.B. Shul'pin, Journal of Molecular Catalysis A: Chemical 189 (2002) 39–66. For parts 1–12 of this series, see Refs. [12–23], respectively.
[2] P. Gallezot, Chemical Society Reviews 41 (2012) 1538–1558.
[3] A. Corma, S. Iborra, A. Velty, Chemical Reviews 107 (2007) 2411–2502.
[4] Y.C. Sharma, B. Singh, Renewable and Sustainable Energy Reviews 13 (2009) 1646–1651.
[5] J. Sepulveda, S. Teixeira, U. Schuchardt, Applied Catalysis A: General 318 (2007) 213–217.
[6] M. Guidotti, E. Gavrilova, A. Galarneau, B. Coq, R. Psaro, N. Ravasio, Green Chemistry 13 (2011) 1806–1811.
[7] E. Poli, N. Biona, J. Barrault, S. Casciato, V. Dubois, Y. Pouilloux, J.-M. Clacens, Catalysis Today 157 (2010) 371–377.
[8] C.I. Keeling, K.N. Slessor, H.A. Higo, M.L. Winston, Proceedings of the National Academy of Sciences of the United States of America 100 (2003) 4486–4491.
[9] K.F. Sibbons, K. Shastri, M. Watkinson, Journal of the Chemical Society Dalton Transactions (2006) 645–661.
[10] D. Veghini, M. Bosch, F. Fischer, C. Falco, Catalysis Communications 10 (2008) 347–350.
[11] H. Kilic, W. Adam, P.L. Alsters, Journal of Organic Chemistry 74 (2009) 1135–1140.
[12] G.B. Shul'pin, J.R. Lindsay Smith, Russian Chemical Bulletin 47 (1998) 2379–2386.
[13] G.B. Shul'pin, G. Süss-Fink, J.R. Lindsay Smith, Tetrahedron 55 (1999) 5345–5358.
[14] G.B. Shul'pin, G. Süss-Fink, L.S. Shul'pina, Journal of Molecular Catalysis A: Chemical 170 (2001) 17–34.
[15] G.B. Shul'pin, G.V. Nizova, Y.N. Kozlov, I.G. Pechenkina, New Journal of Chemistry 26 (2002) 1238–1245.
[16] C.B. Woitiski, Y.N. Kozlov, D. Mandelli, G.V. Nizova, U. Schuchardt, G.B. Shul'pin, Journal of Molecular Catalysis A: Chemical 222 (2004) 103–119.
[17] G.B. Shul'pin, G.V. Nizova, Y.N. Kozlov, V.S. Arutyunov, A.C.M. dos Santos, A.C.T. Ferreira, D. Mandelli, Journal of Organometallic Chemistry 690 (2005) 4498–4504.
[18] D. Mandelli, R.A. Steffen, G.B. Shul'pin, Reaction Kinetics and Catalysis Letters 88 (2006) 165–174.
[19] V.A. dos Santos, L.S. Shul'pina, D. Veghini, D. Mandelli, G.B. Shul'pin, Reaction Kinetics and Catalysis Letters 88 (2006) 339–348.
[20] G.V. Nizova, G.B. Shul'pin, Tetrahedron 63 (2007) 7997–8001.
[21] G.B. Shul'pin, M.G. Matthes, V.B. Romakh, M.I.F. Barbosa, J.L.T. Aoyagi, D. Mandelli, Tetrahedron 64 (2008) 2143–2152.
[22] G.B. Shul'pin, Y.N. Kozlov, S.N. Kholuiskaya, M.I. Plieva, Journal of Molecular Catalysis A: Chemical 299 (2009) 77–87.
[23] G.B. Shul'pin, Y.N. Kozlov, L.S. Shul'pina, T.V. Strelkova, D. Mandelli, Catalysis Letters 138 (2010) 193–204.
[24] V.B. Romakh, B. Therrien, G. Süss-Fink, G.B. Shul'pin, Inorganic Chemistry 46 (2007) 1315–1331.
[25] D. Mandelli, Y.N. Kozlov, C.C. Golfeto, G.B. Shul'pin, Catalysis Letters 118 (2007) 22–29.
[26] Y.N. Kozlov, G.V. Nizova, G.B. Shul'pin, Journal of Physical Organic Chemistry 21 (2008) 119–126.
[27] G.B. Shul'pin, Mini-Reviews in Organic Chemistry 6 (2009) 95–104 (and references cited therein).
[28] G.B. Shul'pin, Organic & Biomolecular Chemistry 8 (2010) 4217–4228 (and references cited therein).
[29] H.-K. Kwong, P.-K. Lo, K.-C. Lau, T.-C. Lau, Chemical Communications 47 (2011) 4273–4275.
[30] G.B. Shul'pin, G.V. Nizova, Y.N. Kozlov, L. Gonzalez Cuervo, G. Süss-Fink, Advanced Synthesis and Catalysis 346 (2004) 317–332.
[31] B.C. Gilbert, J.R. Lindsay Smith, A. Mairata i Payeras, J. Oakes, R. Pons i Prats, Journal of Molecular Catalysis A: Chemical 219 (2004) 265–272.
[32] J.R. Lindsay Smith, B.C. Gilbert, A. Mairata i Payeras, J. Murray, T.R. Lowdon, J. Oakes, R. Pons i Prats, P.H. Walton, Journal of Molecular Catalysis A: Chemical 251 (2006) 114–122.
[33] B.C. Gilbert, J.R. Lindsay Smith, A. Mairata i Payeras, J. Oakes, Organic & Biomolecular Chemistry 2 (2004) 1176–1180.
[34] A.E. Anastasi, P.H. Walton, J.R. Lindsay Smith, W.M.C. Sameera, J.E. McGrady, Inorganica Chimica Acta 361 (2008) 1079–1086.
[35] S. Zhou, X. Chen, C. Qian, Chemical Physics Letters 488 (2010) 44–49.