SHORT PAPER

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Environmentally friendly catalysis using supported reagents: catalytic epoxidation with hydrogen peroxide mediated by iron(II) ions immobilised on γ-alumina[†]

Hassan Hosseini Monfared* **and Mitra Ghadimi**

Department of Chemistry, University of Zanjan, Zanjan 45195-313, Iran

A simple heterogeneous catalyst based on supporting iron(II) ions on γ-alumina was developed and successfully applied to the selective epoxidation of olefins with 35% aqueous H_2O_2 as an oxygen donor in CH_3CN.

Keywords: heterogenous catalyst, hydrogen peroxide, iron ions

Considerable interest continues to surround the search for active and selective catalysts for the epoxidation of olefins under ambient conditions with various oxygen donors such as peroxides.[1-4] The driving force behind catalytic oxidations with hydrogen peroxide is the need for cleaner processes, particularly in fine chemical manufacture. A number of problems, however, hamper its use in oxidation reactions. In addition to the intrinsic danger associated with concentrated H_2O_2 solutions, there is the decomposition reaction catalysed by most transition metals and the need to handle a biphasic system.[5] In this context, the design of new heterogeneous catalysts for liquid-phase oxidation plays an important role. This is not only because they offer the advantage of ease of recovery, but because they also offer the possibility of designing site-isolated redox metal catalysts which may be capable of preventing H_2O_2 decomposition.

During the course of a study to develop a non-Fenton type catalytic system for epoxidation of olefins with 35% H_2O_2 / $FeCl_2$ in a mixture of *N*,*N*-dimethylformamide (DMF) and water, we have found that good conversions could be obtained by careful control of the DMF-H_2O ratio as well as of the catalyst and olefin concentrations. The only disadvantage of this catalytic system was the need for a large excess of oxidant (about 28 equivalents of H_2O_2 per equivalent of olefin), to obtain high conversions in reasonable reaction times. During continuation of this study we have noticed that heterogenisation of iron(II) ion by supporting it on silica gel makes it inactive toward H_2O_2 decomposition.[6] The nature of the support has a profound effect on the catalyst reactivity. Immobilisation of Fe(II) ion on silica gel improved its catalytic activity toward the substrate, but attempted oxidation of some olefins like *cis*- and *trans*-stilbene was not successful. We wish to report here the effective oxygenation of olefins with hydrogen peroxide catalysed by Fe(II) ions immobilised on γ-alumina in acetonitrile in spite of homogeneous Fe(II) and Fe(III) ions which catalyse hydrogen peroxide decomposition.

The catalyst was prepared by stirring a given amount of iron(II) sulfate heptahydrate (0.30 g) and neutral aluminum oxide 90 (Merck) (5.00 g) in methanol (50 ml) for 24h at room temperature. The solvent was removed by filtration through a fritted funnel. The cream coloured solid was subsequently washed with methanol and dried in air. The iron loading was determined by measuring the amount of unloaded $FeSO_4$ in the solvent and the washings by UV/Vis spectroscopy[7] (0.210 mmol $FeSO_4$ / 1g Al_2O_3). Washing studies with methanol, dichloromethane, acetonitrile, and DMF (all of which dissolve free iron(II) sulfate to some extent) confirmed the strong metal ion-surface binding and no detectable iron was removed from the supported reagent. FT-IR spectra of the resulting catalyst and alumina were the same.

In a typical experiment, to a solution of olefin (2.36 mmol) containing supported catalyst (0.40 g, 0.084 mmol Fe^{2+}) in CH_3CN (7.0 ml), an aqueous solution of 35% H_2O_2 (1.20 ml, 13.68 mmol) was added, and the mixture was stirred for the required time at 30 ± 1 °C. At the end of the reaction, the mixture was filtered through a fine fritted funnel and the solid was washed with 3ml of CH_3CN. The mixture of the washings and the filtrate was dried over magnesium sulfate. The conversion of starting olefin was determined by GC. After evaporation of solvent the products were characterised by comparison their ^1H NMR spectra with those reported in literature.[8] Analysis by ^1H NMR of crude norbornene epoxide in a minimum of carbon tetrachloride indicated 40% *exo*-norbornene oxide (resonance at 2.87 ppm) and 50% endo-norbornene oxide (resonance at 3.4 ppm).

Some significant results for several substrates are listed in Table 1. There was no noticeable release of oxygen gas during the reactions. The Al_2O_3-Fe^{2+} catalyst was unchanged at the end of the reactions and almost identical results were observed by repeated oxidation of styrene and cyclooctene after 5 recycles. If either iron(II) or Al_2O_3-Fe^{2+} was omitted, no detectable yields of oxidation products were observed under otherwise identical conditions after 24h. Oxidations of styrene and cyclooctene were examined in different solvents including $CHCl_3$, CH_2Cl_2, CH_3OH, and petroleum ether. The maximum conversion of olefins was achieved in CH_3CN. The reaction does not seem to depend upon a possible peroxymidic acid species which could have been formed as an intermediate upon reaction of H_2O_2 and CH_3CN, since no CH_3CONH_2 was detected at the end of the reactions.[9]

As shown in Table 1, the H_2O_2 / Al_2O_3-Fe^{2+} / CH_3CN system was found to be very efficient for oxidation of different olefins. With 6.8 equivalents of H_2O_2 , olefin conversion varied between 25 and 90% and epoxide yields derived from each olefin between 9 and 90%. It is noteworthy that oxidation of norbornene, cyclooctadiene, cyclooctene, and indene give only the corresponding epoxide. The major products of *cis*- and *trans*-stilbene and styrene oxidations generally result from the cleavage of double bond.

The high conversions with various olefins, the good yields of epoxide obtained at room temperature, the ready availability of the oxidising agent (H_2O_2 diluted in H_2O) as well as the cheap and environmentally benign method make this new *non*-heme system very convenient from a preparative point of view for olefin epoxidation.

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* To receive any correspondence. E-mail: monfared@mail.znu.ac.ir

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Oxidation of various olefins with hydrogen peroxide catalysed by Al_2O_3-Fe^{2+} in CH_3CN (30 °C)[a]

Run	Substrate	Time/h	Conv./%	Product(s)/%
1	Norbornene	24	90	*Exo*-epoxide(40) *Endo*-epoxide(50)
2	Cyclooctadiene	24	50	Monoepoxide(50)
3	Cyclooctene	24	44	Epoxide(44)
4	Indene	24	25	Epoxide(25)
5	*Cis*-stilbene	12	33	*Cis*-epoxide(10) *Trans*-epoxide(10) Benzaldehyde(13)
6	*Trans*-stilbene	24	48	*Cis*-epoxide(4) *Trans*-epoxide(12)
7	Styrene	24	62	Benzaldehyde(40) Diol(12)
8	Cyclohexene	24	70	Epoxide(20) Allylalcohol(37) Allylketone(13)
9	1-octene	24	69	Epoxide(9) Diol(60)

[a]Conditions: olefin (2.36 mmol), Al_2O_3–Fe^{2+} (0.40 g, 0.084 mmol Fe^{2+}), aqueous 35% H_2O_2 (13.68 mmol), CH_3CN (7 ml). Yields based on starting olefin. Conversion determined by GC and product proportions by ^1H NMR.

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References

1 R.A. Sheldon and J.K. Kochi, *Metal Catalyzed Oxidation of Organic Compounds*, Academic Press, New York, 1981, p.271.

2 N. Mizuno, C. Nozaki, I. Kiyoto and M. Misono, *J. Am. Chem. Soc*., 1998,**120**, 9267.

3 J. Rudolph, K.L. Reddy, J.P. Chiang and K.B. Sharpless, *J. Am. Chem. Soc.*, 1997, **119**, 6189.

4 H. Yao and D.E. Richardson, *J. Am. Chem. Soc.*, 2000, **122**, 3220.

5 G. Strukul, Ed., *Catalytic Oxidation with Hydrogen Peroxide as Oxidant*, Kluwer, Dodrecht, The Netherlands, 1992.

6 H.H. Monfared and M. Ghorbani, *Monatsh. Chem*., 2001, **132**, 989.

7 A.D. John, *Analytical Chemistry Handbook*, McGraw-Hill, New York, 1995.

8 *The Sadtler Standard Spectra, NMR*, Sadtler Research Laboratory, Philadelphia (1972).

9 G.B. Payne, P.H. Deming and P.H. Williams, *J. Org. Chem*., 1961, **26**, 659.