Monatshefte für Chemie 132, 989–992 (2001)

Monatshefte für Chemie
Chemical Monthly

Hydrogen Peroxide Oxidation of Hydrocarbons Catalyzed by a Silica Supported Iron Precursor

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Summary. Silica supported iron(II) was found to be an efficient catalyst for oxidation of hydrocarbons with hydrogen peroxide.

Keywords. Catalysts; Hydrocarbons; Hydrogen Peroxide; Iron; Oxidation.

Introduction

The selective oxidation of hydrocarbons continues to be a very important method for the preparation of chemicals in the chemical industry [1, 2]. In addition, for obvious environmental constraints, classical stoichiometric oxidants, such as dichromate or permangenate, should be replaced by new environmentally friendly catalytic processes using clean oxidants like molecular oxygen or hydrogen peroxide.

Most transition metal catalyzed oxidations employ oxidants such as iodosylbenzene, hypochlorite, peracids, or monoperoxosulfuric acid [3, 4]. Attempts to utilize hydrogen peroxide or dioxygen were of rather limited success [5–9] as compared to the high-turnover, high-yield processes using iodosylbenzene. One cause of the failure to achieve better efficiency with hydrogen peroxide results from the interference of radical-producing side reactions [5]. A chain decomposition of hydrogen peroxide occurs along with the free-radical processes associated with the particular substrate [10–12]. We now report the use of silica supported iron(II) as a benign and highly efficient catalyst for the oxidation of hydrocarbons with hydrogen peroxide.

Results and Discussion

In an effort to develop a non-*Fenton* type catalytic system for epoxidation of olefins with 35% hydrogen peroxide we have used iron(II) chloride as a catalyst in a mixture of N,N-dimethylformamide and water. By careful control of the *DMF*-H_2O ratio as well as of catalyst and olefin concentrations, good conversions and moderate to excellent selectivities for the epoxidation of olefins were achieved. However, in order to achieve high conversions at reasonable reaction times, a high excess of

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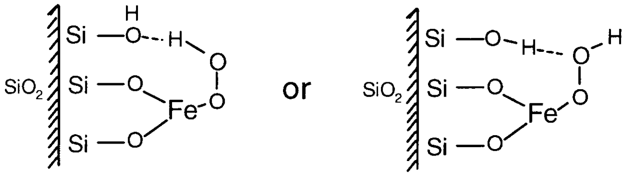
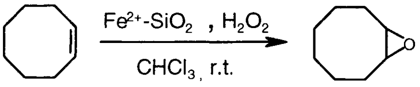


Scheme 1

oxidant was required (*ca.* 28 equivalents of H_2O_2 per equivalent of olefin), which might be considered as a drawback.

The supported catalyst is inexpensive and easily prepared by reaction of iron(II) sulfate with silica gel in methanol. The most important point is the fact that supported iron does not catalyze hydrogen peroxide decomposition. It is postulated that, similar to reported studies [13], in the presence of H_2O_2 an adduct is formed which may be an iron(III)-η^1-hydroperoxide species stabilized by hydrogen bonding between the hydroperoxide ion and the oxygen atom of the silica gel (Scheme 1). The strong metal ion-surface binding is nicely illustrated by simple washing studies which show that methanol, dichloromethane, acetonitrile, and *DMF* (all of which dissolve free iron(II) sulfate to some extent) do not remove any iron from the supported reagent. Interestingly, even after stirring vigorously with water for 4 h only 10% of the iron was washed off the catalyst.

Initial screening of the catalytic activity of the supported iron was carried out by varying the solvent and hydrogen peroxide amount in the epoxidation of cyclooctene at 31°C. The best conditions proved to be chloroform (3.5 cm^3) and 6 mmol hydrogen peroxide together with 0.59 mmol of cyclooctene and 0.20 g of the catalyst. This system gave 100% conversion to cyclooctene oxide in less than 7 h (^1H NMR), corresponding to a turnover number of 33 moles of cyclooctene oxidized per equivalent of iron(II). By increasing the initial amount of cyclooctene, turnover numbers of up to 395 were obtained. It is noteworthy that the oxidation of cyclooctene with one equivalent of H_2O_2 also resulted in 95% conversion. It turned out that hydrogen peroxide decomposition, in spite of homogeneous iron(II) sulfate, was only negligibly catalyzed by supported iron(II) sulfate.



Scheme 2

The $H_2O_2/FeSO_4$-SiO_2 epoxidizing system converted cyclooctene, 1-octene, and cyclooctadiene to the corresponding epoxides with 100% selectivity (Table 1). The main product of the oxidation of cyclohexene with this system was cyclohexen-2-ol. Apparently, the epoxide resulting from the oxidation of styrene is not stable in this oxidation system, and rearrangement to benzaldehyde occurs. Product yields could be increased by longer reaction periods. No iron could be detected in any of the solution phases during the reaction. The stability of the supported $FeSO_4$ catalyst was studied by repeated epoxidation of cyclooctene by hydrogen peroxide.

Table 1. Catalytic oxidation of hydrocarbons using supported iron[a]

Run	Substrate	Products	Yield/%[b]	Reaction time/h
1	cyclooctene	cyclooctene oxide	100	7
2	cyclooctene[c]	cyclooctene oxide	95	7
3	cyclooctene	cyclooctene oxide	41	3
4	1-octene	1-octene oxide	5	24
5	cyclooctadiene	1,2-cyclooctadiene oxide	37	12
6	cyclohexene	cyclohexene oxide	3	3
		cyclohexen-2-ol	21	
7	styrene	benzaldehyde	20	17
8	*trans*-stilbene		0	24
9	tetrahydro-naphtalene	α-tetralol	44	24
10	cyclohexane	cyclohexanone	38	24
11	*n*-heptane	2-heptanol	3	24

[a] Reaction conditions: substrate 0.59 mmol, $CHCl_3$ 3.5 cm^3, $FeSO_4/SiO_2$ 0.20 g, H_2O_2 6 mmol, $T = 31 \pm 1°C$; [b] ^1H NMR yields are based on the starting substrate; [c] 0.59 mmol H_2O_2

After each reaction, the catalyst was removed by filtration, washed, and reused. It showed almost the same catalytic activity after 6 cycles. Tetrahydronaphthalene and cyclohexane can be oxidized effectively with this system to α-tetralol and cyclohexanone, respectively.

Experimental

Olefins and alkanes were obtained from Merck and mostly used without further purification. Styrene and cyclohexene were purified by passing through a short silica column before use. Hydrogen peroxide (H_2O_2, 35% in H_2O, Fluka) was stored at 5°C; its exact concentration was determined volumetrically [14]. Solvents, iron(II) sulfate heptahydrate, and silica gel (0.04–0.063 mm) were purchased from Merck. ^1H NMR spectra were recorded on a JEOL-EX instrument (90 MHz) in $CDCl_3$. IR spectra were run on an Impact Matson-1000 FT-IR spectrometer, and UV/Vis spectra on a Milton ROY 20D spectrophotometer. Thin layer chromatography (TLC) was performed using silica gel polygram SILG/UV 254 plates.

Adsorption of iron(II) on silica gel

$FeSO_4 \cdot 7H_2O$ (193 mg) was loaded onto the silica gel (4.421 g) by stirring in MeOH (50 cm^3) for 24 h at room temperature. The solvent was removed by filtration through a fritted funnel. The cream colored solid was subsequently washed with MeOH and petroleum ether, and the loading (0.090 mmol $FeSO_4$/1 g SiO_2) was determined by measuring the amount of unloaded $FeSO_4$ in the solvent and the washings (UV/Vis spectroscopy, [14]). The supported catalyst was dried under vacuum. The appearance of the FT-IR spectra of the resulting catalyst and silica were almost the same. We believe that the Fe^{2+} ion is exchanged with silica protons and that its interaction with silica surface is nearly as strong as that of H^+.

General procedure for oxidation reactions in the presence of supported catalyst

To a solution of substrate (0.59 mmol) containing supported catalyst (0.20 g) in $CHCl_3$ (3.5 cm^3), an aqueous solution of 35% H_2O_2 (0.5 cm^3, 6 mmol) was added, and the reaction mixture was stirred for an appropriate time at 31 ± 1°C. At the end of the reaction, the mixture was filtered through a 60 cm^3 40F fritted funnel. The solid was washed with 3 cm^3 of the reaction solvent, and the washings were added to the filtrate. After evaporation of the solvent, the molar ratio of the crude products was determined by ^{1}H NMR spectroscopy. The nature of the products was ascertained by comparing their IR and ^{1}H NMR spectra with those of authentic samples.

Acknowledgements

The authors are grateful for financial support from the Research Council of Zanjan University.

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Received January 29, 2001. Accepted (revised) March 5, 2001

Verleger: Springer-Verlag KG, Sachsenplatz 4–6, A-1201 Wien. – Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. – Redaktion: Währinger Straße 38, A-1090 Wien. – Satz und Umbruch: Thomson Press Ltd., New Delhi, India. – Offsetdruck: Manz Crossmedia, A-1051 Wien. – Verlagsort: Wien. – Herstellungsort: Wien. – Printed in Austria.