

Electrocatalytic Epoxidation of Olefins Using Iron(III) Tetraphenylporphyrin Chloride

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Electrocatalytic epoxidation of olefins by using iron-porphyrin complex, iron(III) tetraphenylporphyrin chloride, as a mediator in an acetone aqueous Na₂SO₄ two phase system was performed successfully in an one-compartment cylindrical cell under constant potential condition. The epoxidation reactions have been monitored by gas chromatographic analysis. Optimization of the electrolysis conditions and estimation of the reaction mechanism are discussed.

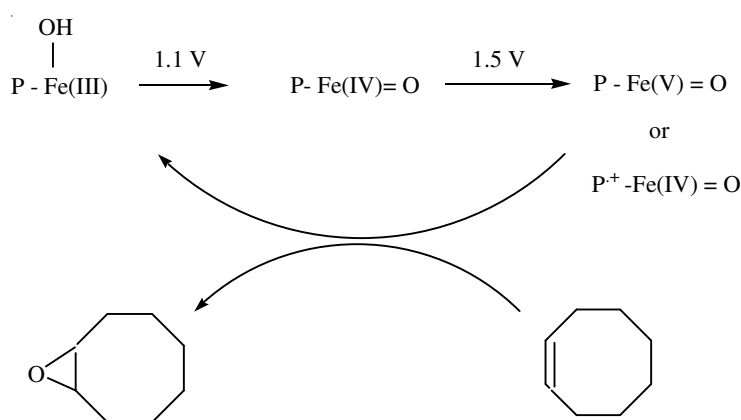
Key Words: Electrocatalytic reaction, Epoxidation, Olefin, Iron-porphyrin.

INTRODUCTION

The cytochromes P-450 are a superfamily of cysteine thiolate ligated heme iron enzymes that activate dioxygen for the insertion or addition of a single oxygen atom into a wide variety of substrates, including alkanes to form alcohols, alkenes to form epoxides, sulfides to form sulfoxides, *etc.* P-450 enzymes are critical to many biological processes including steroid hormone biosynthesis, drug metabolism and the detoxification of xenobiotics¹⁻³. The chemical oxidation of alkene catalyzed metalloporphyrins in mimicking cytochrome P-450 has been studied extensively. Literature oxidations have been carried out almost exclusively by chemical methods in the catalytic reactions. The oxidants, which are also oxygen atom sources, include organic alkyl peroxides, peracids, iodosyl benzene as well as inorganic compounds⁴.

Almost two decades ago, however, Groves and Gilbert⁵ demonstrated the olefin epoxidation could be effected electrochemically. They used an iron porphyrin as the catalyst in solution and water as the oxygen source. Since then, very few reports have appeared describing electrochemical approaches to epoxidation using other iron porphyrin catalysts⁶⁻¹⁰. This dearth of electrochemical efforts probably lies in fact that epoxidation using water as the oxygen source requires that the iron porphyrin catalyst be oxidized to the formal Fe(V) form in order to provide the necessary two oxidizing equivalents.

We described here an electrocatalytic cycle (**Scheme-I**) in which Fe(III)-porphyrin undergoes two-electron electro-oxidation to form O=Fe(V)-porphyrin. This cycle is of special interest since it contains the essential elements of the cytochrome P-450 catalytic cycle: metalloporphyrin catalyst, substrate, reducing equivalents. FeTPP₂Cl, (TPP = tetraphenylporphyrin) in an acetone aqueous Na₂SO₄ two phase system media, have been used for electrocatalytic epoxidation of olefins. The epoxidation reactions have been monitored by gas chromatographic analysis. Optimization of the electrolysis conditions and estimation of the reaction mechanism are discussed.



Scheme-I

EXPERIMENTAL

The electrochemical measurements were recorded on an electroanalyzer system Model Sama 500 (Sama research center, Esfahan, Iran) in a three-compartment electrolysis cell. The electrocatalytic oxidation was carried out in a 50 mL one-compartment cylindrical cell. The working electrode was platinum gauze (170 cm² surface area, 15 mm wire diameter) and a platinum wire was used as the auxiliary electrode, which was separated by a fine glass frit. An Ag/AgCl electrode was used as the reference electrode. An initial background scan was run to check the purity of the reagents and to establish the solvent anodic potential range. The electrochemical measurements were carried out at a thermostated temperature of 25.0 ± 0.1 °C.

Samples were analyzed on a Varian gas chromatography model STAR 3400 equipped with a 10 % OV-101 CWHP 80/100 (2 m × 1/8" SS) and a FID detector. In the temperature program, the initial temperature of 120 °C was held for 3 min, ramped at 10 °C/min to a final temperature of 200 °C and held there for 20 min. A typical chromatogram of the compounds is shown in Fig. 1. Gas chromatography shows that cyclooctene and epoxyoctane appears at a retention time of 1.52 and 3.74 min, respectively.

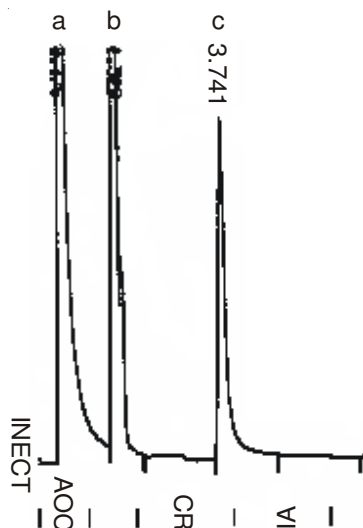


Fig. 1. A typical GC chromatogram of the mixture of cyclooctene (retention time of 1.52) and epoxyoctane (retention time of 3.74) compounds in acetone

All solvents were dried by refluxing for several days over sodium and benzophenone under argon and distilled immediately before use. Purified nitrogen (99.99 %) was used without further treatment. All reagents and solvents used in this study were obtained from Merck & Aldrich Chem. Co. and used without further purification. FeTPPCL was synthesized according to literature methods¹¹. Cyclooctene and cyclohexene were used as the substrate in the electrocatalytic oxidations.

General procedures: A mixture of olefin (1 mmol), FeTPPCL complex (0.05 mmol), 25 mL acetone-water (65:35) and 0.1 M aq. Na₂SO₄ (2 mL) was placed electrolysis cell. The mixture was electrolyzed for different time at a constant potential 1.5 V under gentle stirring at 25 °C. After 3 h of electrolysis, *n*-decane was added to the resulting mixture as an internal standard for GC. 5 μL of the solution was taken for the analysis of the recovered olefin. The gas chromatography was carried out for identification and quantification of products. This was done by comparing the products' retention times and peak areas with those of solutions of known concentrations. For example, gas chromatography shows that cyclooctene appears at a retention time 1.52 min, after 1.5 h of electrolysis, chromatogram of the product (epoxyoctane) exhibits a new peak at a retention time 3.74 min.

RESULTS AND DISCUSSION

Electrocatalytic epoxidation of olefins by FeTPPCL: The electron transfer properties of porphyrin complexes have been extensively reported in the literature¹². Electrochemical properties of FeTPPCL were studied in non-aqueous media by Kadish *et al.*^{13,14}. Electrochemical properties of acetone solution of FeTPPCL have been studied on platinum electrode. Oxidation of FeTPPCL by electrochemical

methods gave two oxidation at $E^{1/2} = 1.14$ and 1.39 V in acetone. In first case, one electron oxidation is being assigned to an Fe(III)/Fe(IV) couple and the other one to an oxidation of the conjugated porphyrin macrocycle or oxidation of Fe(IV) to Fe(V)¹⁵.

Electrocatalytic epoxidation of cyclooctene and cyclohexene with Fe-porphyrin complex, FeTPPCl in an acetone aqueous Na₂SO₄ two-phase system was carried out at 25 °C and a constant potential 1.5 V (Table-1, entry 2) to give the desired epoxy-cyclooctane and epoxy-cyclohexane in 78 and 64 % yield, respectively. The yields of the products were almost compatible with those obtained by chemical epoxidation with iodobenzene as a co-oxidant¹⁶.

TABLE-1
ELECTRO-EPOXIDATION OF CYCLOOCTENE AND
CYCLOHEXENE AT VARIOUS TEMPERATURES

Entry	Temp. (°C)	Yield (%)	
		Epoxy cyclooctane	Epoxy cyclohexane
1	30	65	56
2	25	78	64
3	10	80	70
4	0	75	67
5	-4	20	12
6	-8	0	0

A plausible mechanism is shown in **Scheme-I**. The electrooxidation of Fe(III)-TPPCl is known to form the oxo-ferryl porphyrin^{5,6,9}. Thus, the electro-oxidation at *ca.* 1.1 V is attributed to the formation of TPPFe(IV) = O. Further oxidation at 1.5 V would generate TPPFe(V)=O or TPP⁺Fe(IV) = O. Subsequently, TPPFe(V) = O or TPPP⁺Fe(IV) = O complex would react with olefin to give the corresponding epoxide and TPPFe(III)(OH₂).

Effect of the reaction temperature: The effect of the reaction temperature on the electro-epoxidation was investigated (Table-1). At higher temperatures, (10-30 °C), the yield of epoxy-cyclooctane and epoxy-cyclohexane were slightly decreased (Table-1, entries 1 and 3). At lower temperatures (-4 to -8 °C), the epoxidation reaction did not proceed smoothly (Table-1, entries 5 and 6) because a part of the electrolysis solution became frozen.

Effect of catalyst concentration: The electro-epoxidation was also carried out with a changing amount of the Fe-catalyst (Table-2). The yields decreased significantly when the amount of the catalyst was decreased. These results suggest that in each of the experiments, most of the epoxidation of olefins would occur through oxygen transfer from Fe-oxo complex.

Effect of concentration of supporting electrolyte: The electro-epoxidation of cyclooctene and cyclohexene were carried out with variation of the concentration of Na₂SO₄. The results were summarized in Table-3, with increasing of the concentration of Na₂SO₄ from 0.01 to 0.10 M, yield increased (36 %) as expected.

TABLE-2
ELECTRO-EPOXIDATION OF CYCLOOCTENE AND CYCLOHEXENE
WITH VARIOUS AMOUNTS OF THE CATALYST

Entry	Catalyst (mmol)	Yield (%)	
		Epoxy cyclooctane	Epoxy cyclohexane
1	0.05	78	64
2	0.03	45	38
3	0.02	22	12
4	0.01	10	5

TABLE-3
ELECTRO-EPOXIDATION OF CYCLOOCTENE AND CYCLOHEXENE
WITH AQUEOUS Na₂SO₄ of VARIOUS CONCENTRATIONS

Entry	Na ₂ SO ₄ (M)	Yield (%)	
		Epoxy cyclooctane	Epoxy cyclohexane
1	0.30	77	65
2	0.20	77	64
3	0.10	78	64
4	0.05	56	38
5	0.01	20	18

Effect of additive: It was reported that addition of heterocycle bases such as pyridine or imidazole gives a favourable influence toward the epoxidation of olefins¹⁷⁻¹⁹. These ligands coordinate at the axial position of the iron-porphyrin complexes and cause their conformational change, resulting in improvements of both the reaction rate and selectivity. These facts spurred us to investigate the electro-epoxidation with addition of donor ligands, such as imidazole, N-methylimidazole and pyridine. All attempts, however, failed, showing negative effects of the additives (Table-4). Thus the yields decreased by addition of any of the donor ligands. It is likely that most of these ligands would be dissolved in the aqueous phase and suffers oxidation at the anode to pollute the electrode surface.

TABLE-4
ELECTRO-EPOXIDATION OF CYCLOOCTENE AND CYCLOHEXENE
WITH SEVERAL DONOR LIGANDS

Entry	Additive	Yield (%)	
		Epoxy cyclooctane	Epoxy cyclohexane
1	None	78	64
2	Imidazole	54	35
3	N-Methylimidazole	56	34
4	Pyridine	40	37

Above all, the optimum conditions for the electro-epoxidation were summarized as follows. The electrolysis was carried out in an acetone aqueous Na₂SO₄ (0.1 M)

two-phase system in the presence of 5 mol % of the iron-porphyrin complex at 25 °C. The present electro-epoxidation was successfully applied to cyclooctene and cyclohexene.

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