E2-27: Iron (III) tetraphenyl porphyrin chloride; Fe (III) TPPCl catalysed oxidation of 1,2-dichloroethylene

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Monooxygenase enzymes are of current interest to biochemists and pharmacologists as well as to organic and inorganic chemists. Among these, cytochrome P-450 monooxygenase enzymes have received the most attention, because of their key role in metabolism and their ability to catalyse specific oxidation reactions. These reactions are fundamentally involved in hormone regulation and xenobiotic detoxification. Chemical model systems based on metalloporphyrins have been used to understand the detailed molecular mechanism of the reactions catalysed by cytochrome P-450. The objective of this research is to investigate a model catalytic systems for the oxidation of 1,2-dichloroethylene based on the electrooxidation of iron(III) tetraphenylporphyrin chloride with dioxygen.

Commercially available chloro (tetraphenylporphyrin) iron(III) was used. Spectro grade methylene chloride was distilled with CaH_2 and stored over silica gel before use. The electrolyte tetrabutylammonium tetrafluoroborate was recrystallised from chloroform/hexane. The mixture of cis and trans 1,2-dichloroethylene was freshly distilled before use. Cyclic voltametric experiments were performed in an electrochemical cell with an EC/225 voltametric analyzer and recorded on a X-Y recorder. A glassy carbon electrode, Pt wire and a saturated calomel electrode (SCE) were used as working, counter and reference electrodes respectively. Gas chromatographic (GC) analysis was carried out with a Hewlett Packard model 402 B gas chromatograph with a flame ionization detector. In order to investigate the interaction between Fe(III) TPPCl and 1,2-dichloroethylene in the presence of dioxygen, continuous voltage scan experiments were performed as follows. (1) Fe(III)TPPCl and 1,2-dichloroethylene under N_2, (2) Fe(III)TPPCl under oxygen saturated conditions, (3) Fe(III)TPPCl and 1,2-dichloroethylene under O_2 saturated conditions. In these continuous voltage scan experiments, the potentiostat continuously swept the applied potential between the selected extremes. Cyclic voltamograms were recorded several times during the course of the experiment. The controlled potential bulk electrolysis of the reaction mixture consisting of Fe(III)TPPCl and 1,2-dichloroethylene (with and without O_2) was done at + 1.40 V vs SCE followed by GC.

Electrochemical characterization of Fe(III)TPPCl by cyclic voltametry produced peak potential and peak current characteristics in agreement with the literature reports. Cyclic voltametric experiments also indicated that 1,2-dichloroethylene does not undergo direct electrochemical oxidation. The continuous voltage scan experiments carried out in a solution of 1,2-dichloroethylene and Fe(III)TPPCl under N_2 did not result in any new voltametric features indicating no appreciable reaction between Fe(III)TPPCl and 1,2-dichloroethylene. A similar experiment carried out in a solution of Fe(III) TPPCl under oxygen saturated conditions showed insignificant changes in voltametric behaviour of Fe(III)TPPCl. However, a similar experiment in a solution containing all the 3 components; dioxygen, Fe(III)TPPCl and 1,2-dichloroethylene produced new voltametric peaks at +1.13 V and + 0.38 V. The controlled potential bulk electrolysis (at + 1.4 V) linked to GC indicated the gradual disappearance of the trans isomer preferentially over cis isomer. Further, it was possible to calculate the changes of peak area ratio of cis to trans isomer with time. From this GC, it was apparent that the trans isomer is preferentially involved in the reaction over cis isomer. Therefore, the oxidation reaction is stereoselective when an electric potential is applied. This was confirmed by a control experiment where the electric potential is not applied.

The potential ability of dioxygen to act as a oxygen donor in the oxidation of 1,2-dichloroethylene was demonstrated. The electrocatalytic system involved in this study is based on the electrooxidation of Fe(III)TPPCl. The ability of dioxygen to interact with porphyrin cation radical is an interesting feature in this study.