E2-28: Reductive dehalogenation of 1,2-dichloroethylene catalysed by Cobalt(II)tetraphenylporphyrin [Co(II)TPP]

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Electrochemical reduction of halogenated hydrocarbons is difficult and high negative potentials are required. Metalloporphyrins have been shown to catalyse these reactions through chemically or electrochemically reduced metalloporphyrins. This type of reduction reactions are often carried out in nonaqueous solvents. Cobalt tetraphenylporphyrins are commonly used as the catalysts and the $[Co(I)TPP]^-$ is the catalytically active species. If alkyl or

aryl halides are added to the solution of [Co(I)TPP]$^-$ a reaction occurs that leads to the formation of (TPP)Co(R). The objective of this study is to use Co(II)TPP as the catalyst for the reductive dehalogenation of 1,2-dichloroethylene.

Commercially available Cobalt(II) tetraphenylporphyrin [Co(II)TPP] was used as received. Spectrochemical grade methylene chloride was distilled over calcium hydride. Tetrabutylammonium tetrafluoroborate (TBA.TFB) was used as the electrolyte. The compound, 1,2-dichloroethylene was freshly distilled before use. Cyclic voltametric experiments were conducted 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.

Co(II) tetraphenylporphyrin (6.7 mg) was dissolved in 25 ml of 0.1 M TBA.TFB in dichloromethane. A potential cycle was given from +0.80 V to -1.7 V at a rate of 200 mV/sec and cyclic voltamograms of Co(II)TPP itself were recorded under N_2 saturated conditions. Then, 1,2-dichloroethylene was carefully added to the electrochemical cell in successive 0.3 ml increments and solution was stirred under N_2 before the potential was scanned. The cyclic voltamograms were recorded after each successive addition. A N_2 blanket was kept above the solution throughout the experiment.

Cyclic voltametric characterization of Co(II)TPP in dichloromethane indicated the redox processes of Co(II)TPP. In this regard , 4 peaks were obtained at + 0.61, +0.24, -0.95, and -1.45 V vs SCE. In this study, the reductive electrochemistry of Co(II)TPP was mainly focused. Furthermore, it was confirmed that 1,2-dichloroethylene did not show any electrochemical reaction within the potential range of +0.80 V - -1.70 V vs SCE. The voltametric behaviour of Co(II)TPP in dichloromethane was drastically changed upon addition of 1,2-dichloroethylene under N_2 saturation. (1) On addition of 1,2-dichloroethylene, the first reduction peak of Co(II)TPP became irreversible and the current for the peak was dramatically increased. (2) The current of this peak was increased by increasing concentration of 1,2 dichloroethylene. (3) Further increase in substrate concentration resulted in a small, new voltametric peak and finally catalytic peak was shifted towards

the negative direction. From these results, it is suggested that the [Co(I)TPP]$^-$ species which is electrochemically generated is very reactive toward sufficiently activated halogenated alkenes. Thus, [Co(I)TPP]$^-$ instantaneously reacts with 1,2-dichloroethylene to give an intermediate; $TPPCo^{II}$ (CH=CHCl) which is highly reactive and the reduction of this intermediate should be rapid at this potential thereby regenerating Co(II)TPP at the electrode surface. This probably accounts for the dramatic increase of the peak current.

Catalytic reductive-dehalogenation of 1,2-dichloroethylene is postulated to occur under nitrogen saturated conditions in dichloromethane at negative potentials with Co(II)TPP as the catalyst. This reaction could be postulated as a mimic for anaerobic reductive dehalogenation of halogenated hydrocarbons by cytochrome P-450. These types of studies are important because *in vivo* reduction of halocarbons by cytochrome P-450 has been linked to toxic effects of pesticides such as DDT, chlorinated alkenes and halomethanes.