Formic Acid Formation from the Electrochemical Reduction of Carbon Dioxide Catalyzed by a Rhodium Protoporphyrin in aqueous solution

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The electrochemical conversion of CO₂ into valuable fuels is a promising technique to store intermittent energy, such as wind, solar and nuclear, and facilitate a closed carbon cycle. Here we report the formation of formic acid from the electrochemical reduction of CO₂ catalyzed by rhodium-protoporphyrin in aqueous solution. The formation of formic acid is highly dependent on pH with the highest faradaic efficiency of 50% at pH=3 while it is negligible at pH=1. The theoretical predication indicates that CO should be the main product from the electrochemical reduction of CO₂ catalyzed by rhodium-protoporphyrin as cobalt-protoporphyrin. However, the strong affinity of axial ligands hinders the formation of metal-bonded carboxylate or metal-hydride intermediates leading to the difficulty of the formation of CO or formic acid through the intermediate respectively. The most likely intermediate for the formation of formic acid catalyzed by rhodium-protoporphyrin is phlorin-hydride which is an intermediate protonated the meso carbon of the macrocycle.

Keywords: rhodium-protoporphyrin; CO₂ electrochemical reduction; formic acid; phlorin-hydride

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