



Direct Synthesis of Hydrogen Peroxide in Alcohols: Understanding the Role of organic and inorganic processes with Transient Studies

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1. Introduction

Hydrogen peroxide is frequently used as a green oxidizing agent because it is only producing water in the application processes and avoids additional waste. However it is currently mainly synthesized through the anthraquinone process in which large amounts of toxic organic waste are produced [1]. An alternative route is the direct synthesis from hydrogen and oxygen that has been successfully performed on lab scale [2]. Studies on the effect of solvent have shown for the reaction to work in protic solvents and water only with an increased yield in organic solvents. Especially alcohols have shown enhancing effects on the reaction. Despite seemingly being purely inorganic, further experiments demonstrated different dependencies in relation to hydrogen partial pressure in water and organic solvents which indicates the involvement of the organic solvent in the direct synthesis [3]. The role of the solvent and the mechanism was studied here with different transient methods and alcohols as model compounds. Transient experiment were chosen in this occasion because they allow more in depth understanding of elementary reaction steps in contrast to steady state analysis in which the overall reaction kinetics can be investigated. For these experiments one or more experimental parameters is changed over time to disturb the system and create a transient state.

2. Methods

All reactions were conducted in a co-current trickle bed reactor (30 cm, I.D. 1.5 cm) using 150 mg of 5% Pd/C (Sigma-Aldrich) as catalyst. As conditions $\vartheta=5-15^{\circ}\text{C}$, $p=20$ as well as $\dot{V}_g=4$ ml/min and $\dot{V}_l=1$ ml/min were chosen. During the experiments 5% H₂/CO₂ (AGA Gas) and O₂ (AGA Gas) were dosed with 2 MFC (Brooks) in addition to the solvent which was fed by a peristaltic pump fitted with a 2-way valve to select the solvent feed. Two kinds of experiments were applied: Solvent and Gas-Step experiments. For the solvent step experiments, the system was allowed to reach a steady state in water. After 80 min the solvent feed was switched to the alcohol and every 2 min a sample was taken. The gas step experiments were conducted in two modes: H₂ to O₂ or O₂ to H₂. Before the switch to the other gas, the system was either treated with both methanol or water and gas or for a variable time without solvent. The product concentrations were analyzed via a HPLC (Agilent 1100) fitted with UV-Vis detector and with a second HPLC (Agilent 1100) with RI-Detector. Gas phase concentrations were analyzed via GC (Agilent 6890N) using TCD detection.

3. Results and discussion

Three main observations were found from the gas and solvent step experiments. First it was observed that when switching from water to alcohol the system began to oscillate with declining amplitude regarding to hydrogen peroxide until reaching a steady state. During this period, the corresponding carbonyl of the alcohol was measured with a phase delay. The second observation was achieved from the gas step experiments: the system showed a significantly higher hydrogen peroxide concentration after the switch from oxygen to hydrogen. Concluding it was observed that after the switch from hydrogen to oxygen we could see 2 separate hydrogen peroxide maxima. One being a small short maximum and the other being a large plateau, which lasted up to 3h or more without adding additional hydrogen.

This behavior was not observed when water was used as a solvent. Only a very small concentration of hydrogen peroxide was detected for a few minutes. From this observation we conclude that in the alcohols an additional reaction pathway is opened. The long period of the plateau indicates that in alcohols it was possible to utilize the bulk hydrogen. Taking into account the elevated amounts of carbonyl species, we propose that when alcohols are used as solvent they act as a hydrogen donor in combination with the palladium hydride.

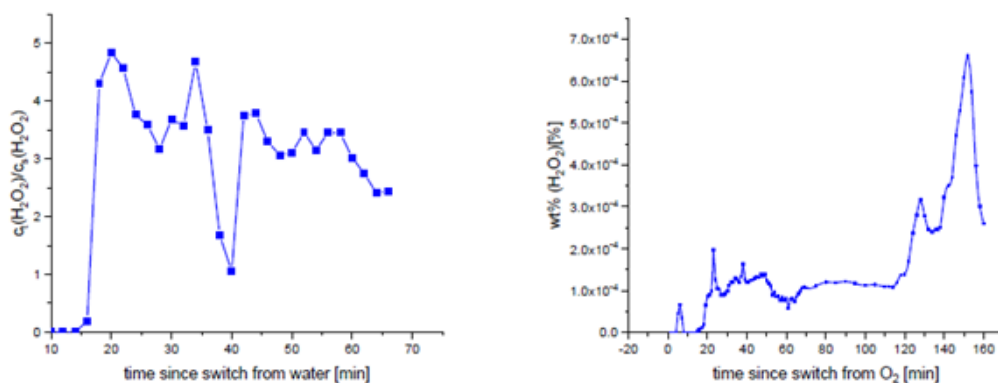


Figure 1. (left) Oscillation pattern after the switch to MeOH (right) Development of hydrogen peroxide concentration after the switch H₂ to O₂ in MeOH.

4. Conclusions

When alcohols are used as solvents in the direct synthesis of hydrogen peroxide, a new reaction pathway is opened. The alcohols act as hydrogen donors for the reduction of oxygen, therefore bulk hydrogen is needed.

References

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