N°283 / OC
TOPIC(s) : Homogenous, heterogenous and biocatalysis / Industrial chemistry

Olefin Epoxidation using Electricity as renewable Power in a Bromide-mediated Electrochemical Process

AUTHORS

Hongyang TANG / KULEUVEN, CMACS, LEUVEN
Dirk DE VOS / KULEUVEN, CMACS, LEUVEN

PURPOSE OF THE ABSTRACT

Introduction: Olefin epoxidation is an important process providing very reactive epoxy motifs to be used in pharmaceuticals, food additives, perfumes and even agrochemicals.1 There is an interest in using electricity as a renewable energy source for forming epoxides. Sargent et al. proposed a chloride-mediated electrochemical synthesis of ethylene and propylene oxides at high current density. However, after the actual electrochemical reaction, the alkali produced in the cathodic chamber needs to be mixed with the chlorohydrin (e.g. 2-Cl-ethanol) formed in the acidic anode chamber. Thus, a separate step is required to obtain ethylene oxide, since the base cannot pass in a sufficient amount through the AEM to enter the anode chamber.2 In a similar, hybrid process in simulated seawater,3 the same problem is encountered. Bromide-mediated protocols have barely received attention.

Our progress: Here we present an electrochemical bromide-mediated olefin epoxidation. Starting with cyclohexene as a model reactant, the kinetics and mechanism are investigated in detail. In the optimal conditions, cyclohexene epoxide is formed with high yield, selectivity and Faradaic efficiency. Addition of extra base is not needed since sufficient alkalinity is generated in situ.

Experimental: We used an undivided glass reactor with two platinum foils as the working and the counter electrode. Epoxide products were identified and quantified via GC and GCMS, with mCPBA as a reference reactant to confirm epoxide formation. Reactions were conducted galvanostatically (7.5mA) for 1-6h at 298K, in a carefully tuned aqueous-organic solvent mix. NaBr was used as a simple electrolyte.

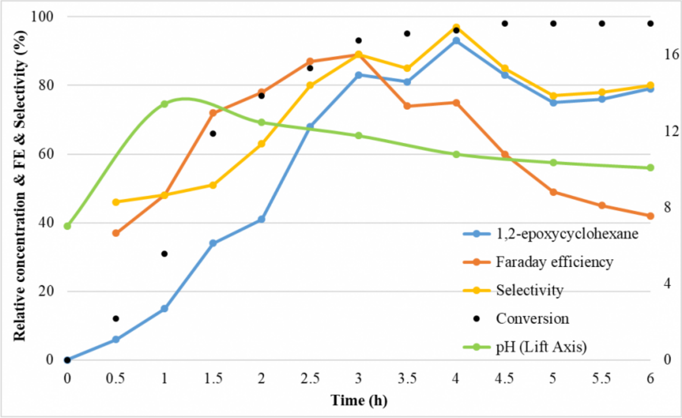
Results and Discussion: We started by selecting optimal electrodes, Pt eventually being most favourable for epoxide formation. Bromide plays a double role, as an electrolyte, but also as a mediator that is easy to oxidize even at moderate anodic voltage. The amount of applied charge and the concentrations of electrolyte and olefin were tuned to maximize efficiency and selectivity. Particularly, the formation of dibrominated compounds is to be avoided, since these present dead-end products.

In a kinetic study, initially the cyclohexene epoxide yield, the Faradaic efficiency and also the epoxide selectivity all increased. At 4h, already > 95 % yield is reached, and this eventually increases up to 98%, with excellent selectivity. The Faradaic efficiency reached its maximum of 89 % after 3h. Interestingly, the pH increases from its initial value of 7, to a high of 13.4 after 1h, and then steadily decreases again towards 10. This ensures that the cathode produces sufficient alkalinity to effect the ring closure towards the epoxide.

As a possible mechanism, we propose that the bromide is initially anodically oxidized to furnish an oxidized 'Br+' species like Br2, HOBr or BrO-, resulting in an electrochemical umpolung. Meanwhile, H2O is reduced on the cathode, and hydrogen and OH- are released. Then HOBr attacks cyclohexene to obtain 2-bromocyclohexanol. Finally, the bromide is eliminated under the alkaline conditions, to obtain the final product epoxycyclohexane. The scope of the method has been documented extensively; besides cyclohexene, a variety of aliphatic and alicyclic olefins, with di- or trisubstituted double bonds can be epoxidized efficiently. However, the compatibility with other functional groups, e.g. alcohols, is limited. We will also in detail report on the epoxidation of a series of biobased terpenic and sesquiterpenic olefins.

Conclusion: The electrochemical, bromide-mediated epoxidation of cyclohexene has the potential to combine a high yield, selectivity, and high Faradaic efficiency. Based on electrochemical kinetics, a reaction mechanism was unraveled, indicating that the formation of epoxide is directly realized under alkaline conditions. This approach, using H2O as source of oxygen atoms, opens up a new synthetic route even for poorly activated olefins.

FIGURES



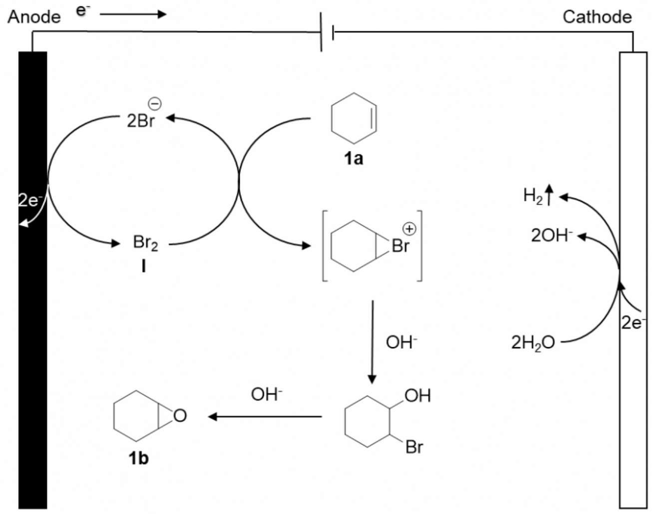


FIGURE 1

Kinetic study

Figure 1. Reaction time and pH

FIGURE 2

Mechanism

Scheme 1. Proposed mechanism for the electrochemical bromine-mediated olefin epoxydation.

KEYWORDS

Epoxidation | Electrochemistry | Olefins | Bromide-mediated

BIBLIOGRAPHY

[1] Nexant Process Evaluation Research Planning (PERP) Report-Propylene oxide, 2018.

[2] Leow, W.R.; Lum, Y.; Ozden, A.; Wang, Y.; Nam, D.H.; Chen, B.; Wicks, J.; Zhuang, T.T.; Li, F.; Sinton, D.; Sargent, E.H., Science 2020, 368, 1228-1233.

[3] Chung, M.; Jin, K.; Zeng, J.S.; Manthiram, K., ACS Catal. 2020, 10, 14015-14023.