International Conference
NEW PERSPECTIVES in SCIENCE EDUCATION

Electrosynthesis of Bromocresol Green – Colorful Experiments for Teaching (not only) Green Chemistry

Christoph Weidmann[1], Jannik Psotta[1], Thomas Waitz[1]

Department of Chemistry Education, Georg-August-Universität Göttingen, Germany[1]

Abstract

Electrosynthetic methods can play an important role in industrial processes for a more sustainable economy based on renewable energies. In order to demonstrate these techniques and the associated benefits, the introduction of electrochemical processes beyond batteries and fuel cells into chemistry classes is very well suited to emphasize the significance of chemistry to overcome the current fossil age.

The electrosynthesis of intensely colored substances (e.g. organic dyes) like bromocresol green are particularly suitable for the implementation in a chemistry course since the distinct color allows the use of only small amounts of substance and therefore short reaction times. Furthermore, the color change can be used to monitor the reaction progress visually as well as (semi-)quantitatively using UV/Vis spectroscopy. The proposed model experiment consists of the electrosynthetic bromination of cresol purple with potassium bromide as bromine source in acetic acid using graphite electrodes at moderate voltages.

We've chosen an electrosynthetic bromination reaction as a model experiment, since important green chemistry principles can be easily demonstrated by generating the bromination agent in-situ: Avoiding the addition of elemental bromine to the reaction mixture clearly establishes a less hazardous synthesis and also obsoletes the need to store large quantities of toxic and corrosive substances on site. Additionally, spectroscopic monitoring of the reaction mixture prevents from accumulating excess bromine and ensures to detect when the reaction is complete, resulting in an efficient use of electric energy.

Keywords: *Electrosynthesis, green chemistry, lab experiment*

1. Introduction

Electrochemistry plays an important role in chemistry classes, for example when different types of batteries (Daniell-Cell, lead-acid battery, Li-Ion battery) are introduced. The possibility to store electric energy does not only affects the daily life of the students, but together with electrolysis and fuel cells, electrochemistry will be a vital part in the ongoing transition of economy and society to a more sustainable future. However, the synthetic use of electrochemical methods is often underrepresented, despite the fact that such techniques are supposed to offer important potential for greener chemistry [1]. Some electrosynthetic processes are under active development or are already commercially used. For example, the electrosyntheis of gluconic acid from glucose is already commercialized as well as the electrochemical reaction of *p*-methoxytoluene and methanol to yield *p*-anisaldehyde [2,3]

For experiments in school or undergraduate lab courses, very few examples are reported, mostly involving the synthesis of alkanes from carboxylic acids using the Kolbe electrolysis [4] or electrooxidative functionalization of carbamates using the Shono-Oxidation [5]. One major drawback of electrosynthetic methods for chemistry classes may be given by the fact, that one colorless product is converted into another, making further analysis needed to show the product formation. Therefore, the use of dyes or pH indicators as substrate for electrochemical reactions has several benefits: The reaction can be monitored with the naked eye as well as spectroscopically and the intense color allows the use of small amounts of substance, ensuring cost-efficient experiments and short reaction times. The experiment proposed in this work extends our previous work on dye bromination [6] to the cresol purple / bromocresol green system which is often used in schools as pH indicator. We focus on the application of the "green chemistry principles" [7,8] to the electrosynthesis of bromocresol green, but additional investigations to determine the indicator transition range and comparison with the reference substance can be conducted to corroborate the identity of the formed product.

2. Experimental

2.1 Electrosynthesis of bromocresol green

In this experiment, bromocresol green is produced by electrosynthesis from cresol purple.

Equipment: Voltage source, cables, stir bar, magnetic stirrer, graphite electrodes, crocodile clips, voltmeter, beakers, spatula, scale.
Chemicals: water, acetic acid (glacial), potassium bromide, cresol purple
Procedure: A saturated potassium bromide solution as electrolyte is prepared as follows: 3 g potassium bromide were mixed thoroughly with 80 mL glacial acetic acid under gentle heating to 40 °C. Excess undissolved potassium bromide was removed by filtration after cooling to room temperature. Additionally, a second solution consisting of 2-5 mg cresol purple in 8 mL water was prepared and mixed with the electrolyte solution. This reaction mixture was electrolyzed for 5 minutes at 5 V using two graphite electrodes. Every 60 to 120 seconds as well as before the start of the reaction, a sample was collected to analyze the product formation in the following experiment.
Observations: The initially pink solution changes its color to red, then orange and later to yellow as shown in Figure 1.

Fig. 1: Experimental Setup (left) and color change of the reaction mixture during electrosynthetic bromination shown on samples taken after 0, 3, 5, 7, 9 and 15 minutes, respectively (right).

Interpretations: At the cathode, water is reduced to hydroxide ions and hydrogen gas. At the anode, bromide ions are oxidized *in-situ* to elemental bromine.

Oxidation: $2\ Br^- \rightarrow Br_2 + 2\ e^-$ Reduction: $2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2$

Bromine then immediately reacts with cresol purple to yield bromocresol green analogous to the established non-electrochemical synthesis procedure [9] as shown in Figure 2.

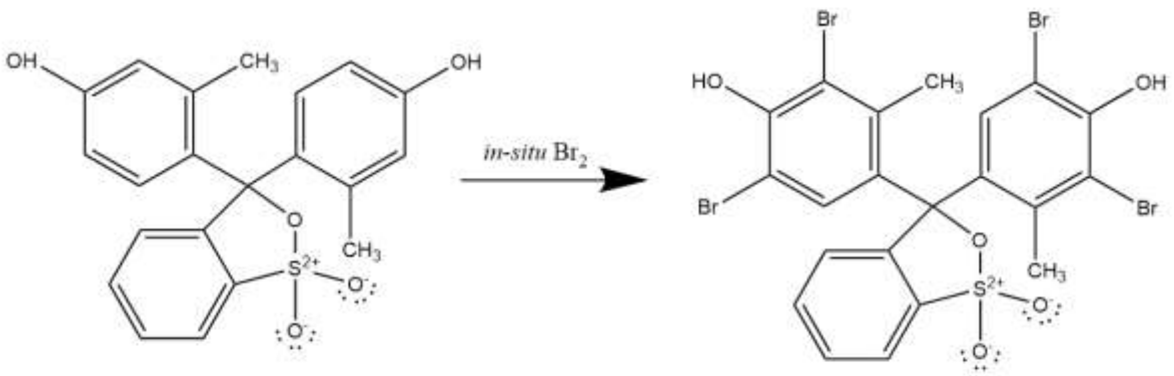

Fig. 2: Reaction of cresol purple with bromine (both shown in protonated form).

2.2 Monitoring the reaction progress using UV/Vis spectroscopy

In this experiment, the collected samples were analyzed using spectroscopic techniques. This can be either done using photometers providing only the wavelength of the adsorption maximum or spectrometers with acquisition of the whole spectrum data.

Equipment: Spectrometer, Cuvettes, Pipettes
Chemicals: Samples from previous experiment, bromocresol green solution for reference, glacial acetic acid and potassium bromide for blank measurement and to dilute if necessary.
Procedure: The procedure depends on the specific spectrometer. Typically, it includes a blank measurement of the electrolyte solution (acetic acid, water and potassium bromide) and dilution of the samples to give suitable absorbance readings.
Observations: The adsorption spectra change with ongoing electrolysis time as shown in Figure 3. An absorption band at ~530 nm decreases with time, while a new absorption band at ~450 nm increases in intensity.

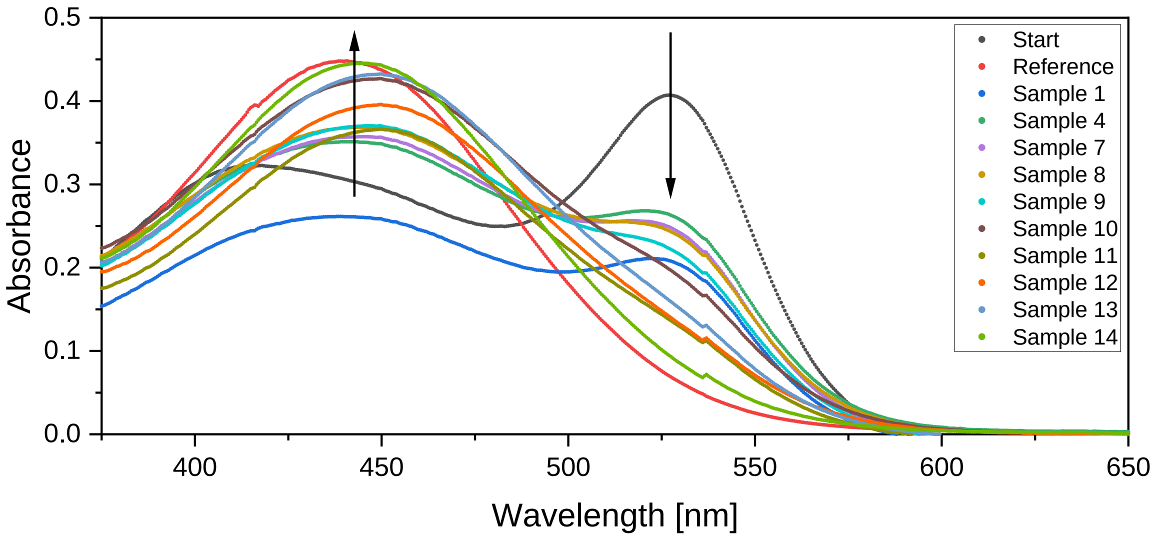

Fig. 3: Absorption spectra of reference sample (bromocresol green in red) and samples taken during the bromination reaction.

Interpretations: By comparison with the sample before electrolysis, the absorption at 530 nm can be assigned to the starting material cresol purple. The appearing absorption band at 450 nm is attributed to the product which can be confirmed using bromocresol green as reference. According to the Beer-Lambert Law the extinction displayed in this graph is directly proportional to the concentration of cresol purple and bromocresol green, respectively and therefore, a decrease of the concentration of cresol purple and a simultaneous increase of the concentration of bromocresol green can be confirmed. Furthermore, no intermediate products can be found in the absorption spectra.
It should be noted, however, that the molar attenuation coefficient for both substances is not identical, so that the concentrations of both dyes cannot be directly compared quantitatively with each other.

3. Didactical considerations

This experiment is dedicated to show the benefits of electrosynthetic methods for lab courses. As stated earlier, a short reaction time and the significant color change during bromination ensures that this procedure can be included in a chemistry lesson. Further advantages are the use of low-cost chemicals with low toxicity.

Both, the conventional synthesis as well as this method can be assessed based on the green chemistry principles. When provided with information about the non-electrochemical synthesis of bromocresol green, an indicator dye they are maybe used to from acid/base chemistry, the students can identify which of the twelve green chemistry principles apply to this process. Possible answers for the conventional synthesis via reaction of cresol purple with added bromine in acetic acid at room temperature could include:

Safe(r) solvents and auxiliaries: Acetic acid can be considered as an environmentally friendly solvent. While being corrosive and acidic, it is non-toxic and biodegradable. No further auxiliaries are needed.

Design for Energy efficiency: The reaction itself can be carried out under ambient conditions without energy demand for heating and cooling.

Despite these green chemistry principles, the students can easily identify bromine as a toxic und potentially hazardous chemical. Due to previous experiments in chemistry lessons, they should know the appropriate safety precautions for handling bromine (working under the fume hood, wearing gloves, disposal of excess bromine with sodium thiosulfate) and consider it to be the least green part of this synthesis. This leads to the following additional green chemistry principles that can be achieved by electrosynthesis:

Less hazardous chemical syntheses: The bromine used for the synthesis of bromocresol green is generated *in-situ* by electrolysis of a bromide solution and immediately reacts with the substrate to give the desired product only. Thus, the risk for possible pollution of the environment is dramatically reduced, since bromine doesn’t have to be transported or stored.

Real-time analysis for prevention of hazardous substances: The spectroscopic monitoring of cresol purple content in the reaction mixture allows for precise control of the reaction time. Therefore, no accumulation of hazardous reagents occurs, if the electrosynthesis is stopped when cresol purple is consumed completely.

4. Conclusion

In conclusion, the presented experiment provides a facile way to introduce electrosynthetic methods into chemistry classes. It provides several opportunities to discuss green chemistry in the lesson and to demonstrate how the combination of *in-situ* generated bromine and the spectroscopic investigations can lead to greener processes. Furthermore, the experiment can be easily extended by determining the indicator properties of the synthesized dye, showing a transition from yellow in strongly acidic media, to green and finally blue at pH > 5.4. Due to the content of acetic acid in the reaction solution, the system is buffered, so that pH changes upon addition of a basic solution do not occur abruptly and allow students to precisely adjust the acidity to observe the gradual color change.

References

[1] Frontana-Uribe, B. A., Little, R. D., Ibanez, J. G., Palma, A., Vasquez-Medrano, R. (2010). Organic electrosynthesis: a promising green methodology in organic chemistry. *Green Chem.* 12, 2099-2119
[2] Cardoso, D. S. P., Šljukić, B., Santos, D. M. F., Sequerira, C. A. C (2017). Organic Electrosynthesis: From Laboratorial Practice to Industrial Applications. *Org. Process Res. Dev.* 21, 1213-1226
[3] Leech, M. C., Garcia, A. D., Petti, A., Dobbs, A. P., Lam, K. (2020). Organic electrosynthesis: from academia to industry. *React. Chem. Eng.* 5, 977-990
[4] Becker, H.-J. (1999). Ethandarstellung im Schulversuch. *Chemkon* 6, 26
[5] Goes, S. L., Nutting, J. E., Hill, N. J., Stahl, S. S., Rafiee, M. (2022). Exploring Electrosynthesis: Bulk Electrolysis and Cyclic Voltammetry Analysis of the Shono Oxidation. *J. Chem. Educ.* 99, 3242-3248
[6] Lanfermann, P., Weidmann, C., Schüler, T., Waitz, T. (2021). Bromination of Fluorescein – A Facile Model Experiment for Electrosynthesis in Chemistry Classes. *Conference Proceeding. New Perspectives in Science Education 10th Edition 2021*
[7] Anastas, P. T.; Warner, J. C. Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30
[8] https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html (retrieved 2023-01-15)
[9] Orndorff, W. R., Purdy, A. C. (1926). Meta-Cresolsulfonphtaleine, 3,6-Dimethylsulfonefluoran and some of their derivatives. *J. Am. Chem. Soc.* 48, 2212-2221