OXIDAÇÕES ELETROQUÍMICAS DE SUBSTÂNCIAS ORGÂNICAS USANDO COMO CATALISADOR UM NOVO AQUACOMPLEXO DIARSÍNICO DE RUTÊNIO (II)

ELECTROCHEMICAL OXIDATIONS OF ORGANIC SUBSTANCES USING A NEW RUTHENIUM (II) DIARSENIC AQUACOMPLEX AS CATALYST

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RESUMO

Várias funções orgânicas podem sofrer reações de oxidação e a indústria química procura desenvolver cada vez mais processos que se ajustam na conduta da chamada Química Verde na busca de processos mais sustentáveis. Os processos eletroquímicos de transferência de elétrons usando complexos metálicos surgem assim como uma alternativa importante nesses processos oxidativos uma vez que exploram muitas reações em meio aquoso e utilizam-se de quantidades catalíticas do complexo. O objetivo deste trabalho foi testar a habilidade como eletrocatalisador de um novo aquacomplexo diarsênico de rutênio (II), $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ ($\text{L}=\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$; $(\text{totpy})=4'-(4\text{-toluyl})-2,2':6',2''\text{-tripiridina}$), em experimentos de eletroxidação de substâncias orgânicas de diferentes funções. As eletroxidações foram conduzidas sob potencial constante de +1,00 V (vs ECS), em solução 7:3 tampão fosfato:t-butanol, pH 8,1, com a proporção de 1,00 mmol.L⁻¹ do aquacomplexo $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ para 50,00 mmol.L⁻¹ de cada substrato orgânico. As substâncias orgânicas de partida oxidadas e os respectivos produtos obtidos foram o álcool benzílico (benzaldeído), benzaldeído (ácido benzóico), éter benzilbutílico (benzaldeído e ácido benzóico) e 1-feniletanol (acetofenona). Observou-se reações seletivas e com bons rendimentos para os produtos. O processo eletroquímico utilizado revelou algumas vantagens frente a outros métodos oxidativos clássicos, como os biológicos e os oxidantes inorgânicos, ressaltando-se a rapidez, a possibilidade de utilizar meio aquoso nas reações, a seletividade na formação dos produtos e a possibilidade de se usar pequena escala de catalisador.

Palavras-chave: complexo metálico, eletrocatalise, eletroxidação, funções orgânicas, rutênio.

ABSTRACT

Various organic functions can undergo oxidation reactions, and the chemical industry increasingly seeks to develop processes based on the Green Chemistry approach in the search for more sustainable practices. Electrochemical electron transfer processes using metal complexes thus appear as an important alternative in these oxidative processes since they exploit numerous reactions in aqueous media and use catalytic amounts of the complex. The purpose of this work was to test the electrocatalytic ability of a new ruthenium (II) diarsenic aqua complex, $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ ($\text{L}=\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$; $(\text{totpy})=4'-(4\text{-tolyl})-2,2':6',2''\text{-terpyridine}$), in electrooxidation experiments of organic substances with different functions. The experiments were conducted at a constant potential of +1.00 V (vs ECS) in a solution of 7:3 phosphate buffer: t-butanol, pH 8.1, with a ratio of 1.00 mmol.L⁻¹ of the aqua complex $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ to 50.00 mmol.L⁻¹ of each organic substrate. The oxidized organic starting materials and the respective products obtained therefrom were benzyl alcohol (benzaldehyde), benzaldehyde (benzoic acid), benzyl butyl ether (benzaldehyde and benzoic acid) and 1-phenylethanol (acetophenone). Selective reactions with good yields for the products were observed. The electrochemical process used here revealed some benefits over other classic oxidative methods, such as biological advantages and inorganic oxidants, emphasizing the speed, the possibility of using aqueous media in the reactions, selectivity in the formation of products, and the possibility of using small amounts of catalyst.

Keywords: metal complex, electrocatalysis, electrooxidation, organic functions, ruthenium.

1. INTRODUCTION:

Over the past two decades, investigations and applications of metal complexes in catalytic reactions have increased significantly in academic research and in the chemical industry, largely due to the selectivity exhibited by most of these reactions (Wang *et al.*, 2019), and more recently in the search for more sustainable processes that align with some of the principles of Green Chemistry (Song *et al.*, 2017).

Research on the subject has shed increasing light on the process that takes place between the substrate and the metallic complex (Thompson *et al.*, 1984; Nunes *et al.*, 2008; Roudesly *et al.*, 2017). In many cases, this has enabled the sequential steps of the stages of reactions to be determined and intermediate compounds to be identified, following changes in the oxidation state of the complex during the catalytic process and providing quantitative descriptions of the metal-substrate coupling (Efimov & Streelets, 1990; Manikandan *et al.*, 2015; Dhawa *et al.*, 2018).

Among the metal complexes used in the indirect electrooxidation of organic compounds, the ones that stand out are the high oxidation state polypyridine oxo/aqua complex systems that are widely used as electrochemical mediators in the transformation of organic substrates (Carrijo & Romero, 1994; Seok & Meyer, 2005; Tong & Thummel, 2016). The application of a suitable potential enables the transformation of an aqua into an oxo complex. This, in turn, oxidizes the organic substrate in aqueous medium, and is reduced to aqua complex, maintaining the catalytic cycle. Ruthenium complexes usually preserve their integrity in solution because the nature of ruthenium allows for a reversible electron transfer without ligand exchange (Seddon & Seddon, 1984).

Terpyridine ligands such as 2,2':6',2''-terpyridine and its substituted derivatives are often employed in the preparation of ruthenium complexes, rendering the complex highly stable against the loss of these ligands (Meyer, 1984; Tse *et al.*, 2005; Ezhilarasu *et al.*, 2017). Diarsenic and diphosphinic bidentate ligands also reportedly offer some advantages over their monodentate analogues by allowing for better control of the coordination number and stereochemistry of the resulting complex and by decreasing intra- and intermolecular exchange processes (Chaudret *et al.*, 1988; Gao *et al.*, 1996). It has been proposed that the hydrophobic

nature of arsines and phosphines makes it difficult to solvate the active oxo center of the complex to which it is bonded. Thus, in electrocatalytic reactions, upon leaving the aqueous phase, the substrate enters the non-solvated region of the active site ($\text{Ru}^{\text{IV}}=\text{O}$); this proximity facilitates the catalytic effect of the complex (Marmion & Takeuchi, 1988; Tong & Thummel, 2016).

Some systematic electrocatalytic studies conducted by our research group on organic substrates have shown that ruthenium polypyridine oxo/aqua complexes mixed with phosphines or arsines were more selective than those containing only polypyridines as ligands (Lima *et al.*, 1998; Sussuchi *et al.*, 2006). Therefore, it was proposed to test the electrocatalytic ability of a ruthenium terpyridine aqua complex containing an innovative combination with a diarsenic bidentate ligand (Figure 1): $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ ($\text{L}=\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$; ($\text{totpy}=4'-(4\text{-tolyl})-2,2':6',2''\text{-terpyridine}$), in electrooxidation experiments of organic substances with different functions in homogeneous aqueous phase.

Figure 1. Chemical structure of ruthenium (II) diarsenic aqua complex $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$.

2. MATERIALS AND METHODS:

2.1. Reagents and Solvents

Double distilled water was prepared by treating distilled water with an alkaline solution of potassium permanganate (KMnO_4), which was then distilled (Morita & Assumpção, 2007). Ethyl ether was previously distilled in sulfuric acid medium in order to remove impurities (Morita & Assumpção, 2007). Dichloromethane was dried on an aluminum trioxide column (Al_2O_3) for the cyclic voltammetry experiments. All the other reagents and solvents, from Merck, Aldrich, Mallinckrodt and Sigma, were used in their

commercial form (P.A.), without further purification. A mixture of salts, $\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$, with ionic strength of 0.25 mol.L^{-1} (phosphate buffer) in a solution of 70:30 mL of double distilled water:t-butanol was used for the preparation of a solution with pH 8.1. This pH level for the phosphate buffer solution was measured directly by a pH meter and is therefore an apparent pH value.

2.2. Equipment

The electrochemical studies were carried out at atmospheric temperature and pressure in a FAC-200 A potentiostat/galvanostat coupled to an Intralab current data logger. The electrooxidation experiments were carried out in a two-compartment electrochemical cell containing saturated calomel as reference electrode, and a platinum plate (1.00 cm^2 area, 0.20 cm thickness) as auxiliary electrode inside a sintered glass tube. The working electrode was a platinum mesh electrode with 164.00 cm^2 of area and a wire diameter of 0.16 mm . ^1H NMR spectra were recorded in Bruker AC-80 nuclear magnetic resonance spectrometer (80MHz) using deuterated chloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as internal standard (0 ppm on the δ scale). The CG analysis was performed in a Varian 3400 gas chromatograph equipped with a flame ionization detector (FID), using OV-17 Chrom W-HP (3% in Chromosorb W, 80-100 mesh) and Carbowax 20M (10% in Chromosorb W, 80-100 mesh) metal columns, both 2.00 m long and 3.00 mm in diameter, and the values obtained were compared with commercially available standards.

2.3. General Method of Electrochemical Oxidations

All the experiments were performed at ambient temperature and pressure in a 7:3 phosphate:t-butanol buffer solution at pH 8.1. The ratio of the concentrations was 1.00 mmol.L^{-1} of the diarsenic aqua complex $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ to $50.00 \text{ mmol.L}^{-1}$ of the organic substrates. After sufficient charge had passed through to oxidize the aqua complex ($\text{Ru}^{\text{II}}\text{-OH}_2 \rightarrow \text{Ru}^{\text{IV}}\text{=O}$) dissolved in the aqueous medium with the solution under stirring, the organic substrate was added and a sufficient amount of charge (Coulombs) was passed to trigger the desired reaction or until the current dropped to values close to the residual currents. At the end of each electrooxidation process, the pH of the solution was raised to approximately 10 by adding an aqueous solution of 1.00 mol.L^{-1} of sodium

hydroxide (NaOH) and the organic phase was extracted five times with portions of 5 mL of ethyl ether. For the experiments leading to benzoic acid (as either a product or a byproduct of the oxidation reaction), the remaining aqueous phase was acidified with hydrochloric acid concentrated to a pH level of about 2.0, and another extraction was carried out with ethyl ether. After evaporation of the solvent, the products were identified and the yield of the reactions was calculated by means of gas chromatography, using a known amount of cyclohexanol as an internal standard, or weighed material, melting point and/or ^1H NMR.

2.4. Synthesis of the ruthenium (II) diarsenic aqua complex $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ ($\text{L}=\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$) (totpy=4'-(4-tolyl)-2,2':6',2''-terpyridine)

The complete synthesis of diarsenic aqua complex $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$, with an innovative combination of a substituted terpyridine ligand (totpy) and a bidentate arsine ligand (L), involved three steps, based on the $[\text{Ru}(\text{OH}_2)_3\text{Cl}_3]$ complex, which is described in the literature (Batalini & De Giovani, 2019).

3. RESULTS AND DISCUSSION:

Table 1 describes the electrochemical oxidation experiments of organic substances with different functions. The oxidations were performed at pH 8.1 because of the better reversible behavior of the $\text{Ru}^{\text{IV/III}}\text{-Ru}^{\text{III/II}}$ redox pairs of the complex, which was revealed in the cyclic voltammetry experiments in aqueous medium when the complex was characterized (Batalini & De Giovani, 2019). The applied potential chosen for all the electrooxidation experiments was $+1.00 \text{ V}$ (vs ECS). This potential, which is higher than the half-wave potential of the $\text{Ru}^{\text{IV/III}}$ redox pair of the aqua complex at pH 8.1, suffices to generate the oxo complex from the aqua complex. The results described in Table 1 indicate reactions that behaved selectively in the formation of a single product. This selectivity was particularly visible in the oxidation experiments of benzyl alcohol and 1-phenylethanol, where the formation of benzoic acid was not observed in the process. In these two experiments, there appeared to be a control that explains this non-formation of benzoic acid, given that benzaldehyde was oxidized to benzoic acid under the same reaction conditions. Thus, the selectivity observed here appears to be a combination of the control of the number of Coulombs applied in the reaction and the excess of substrate during oxidation, when the oxo complex was preferentially oxidized, instead of the

product undergoing subsequent oxidation.

Table 2 describes the data obtained in some electrooxidation processes of organic substrates, in the same conditions as those of the results presented in Table 1, albeit in the absence of the aqua complex $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$. Note that there was practically no oxidation of the organic substrates without the presence of the ruthenium aqua complex synthesized as catalyst. These experiments appeared to function as a direct electrooxidation process of the substrate by the electrode; the applied potential of +1.0 V was insufficient to trigger oxidation. A comparison of the results obtained in the "blank" experiments (Table 2) with the substrates listed in Table 1 clearly shows the importance of the role of the ruthenium oxo/aqua complex system in the electron transfer process, which leads to the formation of products with much higher yields and greater selectivity in the formation of a single product, at lower potentials than that required for the direct oxidation of the substrate by the electrode.

4. CONCLUSIONS:

This study demonstrates the importance of using metallic complexes as electrocatalytic systems in organic reactions. The four organic substances underwent selective oxidation against the new diarsenic aqua complex employed here in a homogeneous aqueous phase. The yields of the catalytic electrooxidation processes varied from good to excellent in the electrolytic processes that did not require bond breaking (benzylbutyl ether), which follows the hydride abstraction step. In addition to the advantages of this process, the use of electrooxidation in an aqueous system such as the one used in this research contributes to render the chemical process less aggressive to the environment.

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6. REFERENCES:

1. Batalini, C.; De Giovani, W. F. *Periódico Tchê Química*, **2019**, 16, 130.
2. Carrijo, R. M.; Romero, J. R. *Synth. Commun.*, **1994**, 24, 433.
3. Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.*, **1988**, 86, 191.
4. Dhawa, U.; Zell, D.; Yin, R.; Okumura, S.; Murakami, M.; Ackermann, L. *Journal of Catalysis*, **2018**, 364, 14.
5. Efimov, O. N.; Streelets, V. V. *Coord. Chem. Rev.*, **1990**, 99, 15.
6. Ezhilarasu, T.; Sathiyaseelan, A.; Kalaichelvan, P. T.; Balasubramanian, S. *Journal of Molecular Structure*, **2017**, 1134, 265.
7. Gao, J. X.; Wan, H. L.; Wong, W. K.; Tse, M. C.; Wong, W. T. *Polyhedron*, **1996**, 15, 1241.
8. Lima, E. C.; Fenga, P. G.; Romero, J. R.; De Giovani, W. F. *Polyhedron*, **1998**, 17, 313.
9. Manikandan, R.; Anitha, P.; Prakash, G.; Vijayan, P.; Viswanathamurthi, P.; Butcher, R. J.; Malecki, J. G. *J. Molec. Catalysis A: Chemical*, **2015**, 398, 312.
10. Marmion, M. E.; Takeuchi, K. J. *J. Chem. Soc., Dalton Trans.*, **1988**, 2385.
11. Meyer, T. J. *J. Electrochem. Soc.*, **1984**, 131, 221-C.
12. Morita, T.; Assumpção, R. M. V. *Manual de soluções, reagentes e solventes*, 2 ed., São Paulo: Ed. Blucher, 2007.
13. Nunes, G. S.; Alexiou, A. D. P.; Toma, H. E. *Journal of Catalysis*, **2008**, 260, 188.
14. Roudesly, F.; Oble, J.; Poli, G. *J. Molec. Catalysis A: Chemical* **2017**, 426 - Part B, 275.
15. Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*, New York: Elsevier, 1984.
16. Seok, W. K.; Meyer, T. J. *Inorganic Chemistry*, **2005**, 44, 3931.
17. Song, Q. W.; Zhou, Z. H.; He, L. N., *Green Chem.*, **2017**, 19, 3707.
18. Sussuchi, E. M.; Lima, A. A.; Giovani, W. F. *Journal of Chemical Catalysis A, Chemical*, **2006**, 259, 302.
19. Thompson, M. S.; De Giovani, W. F.; Moyer, B. A.; Meyer, T. J. *J. Org. Chem.*, **1984**, 49, 4972.
20. Tong, L.; Thummel, R. P. *Chemical*

Science, **2016**, 7, 6591.

21. Tse, M. K.; Klawonn, M.; Bhor, S.; Doebl, C.; Anilkumar, G.; Hugl, H.; Maegerlein, W.; Beller, M. *Organic Letters*, **2005**, 7, 987.

22. Wang, B.; Duke, K.; Scaiano, J. C.; Lanterna, A. E. *Journal of Catalysis*, **2019**, 379, 33.

Table 1. Electrooxidation of organic substances in 7:3 phosphate buffer:t-butanol solution, pH 8.1, using as catalyst the diarsenic aqua complex $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ ($L=Ph_2AsCH_2CH_2AsPh_2$), ($totpy=4'-(4-tolyl)-2,2':6':2''-terpyridine$).

Substrate	I_i / I_f (mA)	Time (h)	% Applied charge	Product (s)	Yield (%) ^a
benzyl alcohol	17/11	6	100 ^b	benzaldehyde	90
benzaldehyde	14/2	14	100 ^b	benzoic acid ^d	46
benzylbutyl ether	12/4.8	14.5	100 ^c	benzaldehyde	18
				benzoic acid ^d	20
1-phenylethanol	11/5	8.5	100 ^b	acetophenone	83

^a Yield calculated based on the charge applied (in Coulombs) (electric yield).

^b Percentage of Coulombs for a process involving two electrons.

^c Percentage of Coulombs for a process involving four electrons.

^d Melting point obtained: 119-121 °C (literature: 121-122 °C); ¹H RMN (δ , $CDCl_3$): 12.0 (s, 1H); 8.20-8.10 (m, 2H) and 7.60-7.50 (m, 3H).

Table 2. Electrooxidation of organic substances in 7:3 phosphate buffer:t-butanol solution, pH 8.1, in the absence of diarsenic aqua complex $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ ($L=Ph_2AsCH_2CH_2AsPh_2$), ($totpy=4'-(4-tolyl)-2,2':6':2''-terpyridine$) (blank experiments).

Substrate	I_i / I_f (mA)	Time (h)	% Applied charge ^a	Product	Yield (%) ^b
benzyl alcohol	12/0.3	4	3.4	benzaldehyde	01
benzaldehyde	5/0.1	15	3.6	benzoic acid ^c	02
1-phenylethanol	10/0.2	17	4.5	acetophenone	04

^a Percentage of Coulombs for a process involving two electrons.

^b Yield calculated based on the charge applied (in Coulombs) (electric yield).

^c Melting point obtained: 119-121 °C (literature: 121-122 °C); ¹H RMN (δ , $CDCl_3$): 12.0 (s, 1H); 8.20-8.10 (m, 2H) and 7.60-7.50 (m, 3H).