

ELECTROOXIDATION OF ORGANIC COMPOUNDS USING SOME PRINCIPLES OF GREEN CHEMISTRY¹

ELETROOXIDAÇÃO DE COMPOSTOS ORGÂNICOS USANDO ALGUNS PRINCÍPIOS DA QUÍMICA VERDE

Claudemir Batalini² e Wagner Ferraresi De Giovani³

ABSTRACT

It has been shown that ruthenium polypyridyl aqua complexes have basically the same electrochemical behavior in weakly coordinating organic solvents, such as methylene chloride and acetone, as in water. Therefore, their use in electrocatalytic processes in water, as they have been conducted in an ecologically cleaner system, they can bring significant benefits for mankind, as well as nature and economy. In this sense, the new ruthenium aqua complex containing diphosphine and polypyridine as ligands, $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ ($L=Ph_2PCH_2CH_2PPh_2$); ($totpy=4'-(4-tolyl)-2,2':6',2''-tripyrindine$), was used as catalyst at pH 8.1 in homogeneous electrooxidation of benzyl alcohol, benzaldehyde, benzylbutyl ether and 1-phenylethanol.

Keywords: Metal complex, electrocatalysis, green chemistry, organic functions, ruthenium.

RESUMO

Aqua complexos de rutênio contendo polipiridinas como ligantes têm, fundamentalmente, o mesmo comportamento eletroquímico em solventes orgânicos coordenantes fracos, como diclorometano e acetona, e em água. Assim, o uso desses complexos em processos eletrocatalíticos, em água, sistema ecologicamente limpo, pode ser benéfico para o homem, a natureza e a economia. Nesse sentido, o novo aqua complexo de rutênio com ligantes polipiridina e difosfina $[Ru(L)(totpy)(OH_2)](ClO_4)_2$ ($L=Ph_2PCH_2CH_2PPh_2$); ($totpy=4'-(4-toluil)-2,2':6',2''-tripiridina$), foi usado como catalisador, em pH 8,1, em eletrooxidação do álcool benzílico, benzaldeído, éter benzilbutílico e 1-feniletanol.

Palavras-chave: Complexo metálico, eletrocatalise, química verde, funções orgânicas, rutênio.

1 Pesquisa de Pós-Graduação - Doutorado.

2 Doutor em Química Orgânica - Professor Titular da Universidade Federal de Mato Grosso - UFMT/CUA - Pontal do Araguaia - MT. E-mail: pirapotimao@msn.com. ORCID: <https://orcid.org/0000-0002-5915-0850>

3 Professor Titular (aposentado) da Universidade de São Paulo - USP/Ribeirão Preto - SP. E-mail: wfdgiova@usp.br. ORCID: <http://orcid.org/0000-0003-3417-348X>

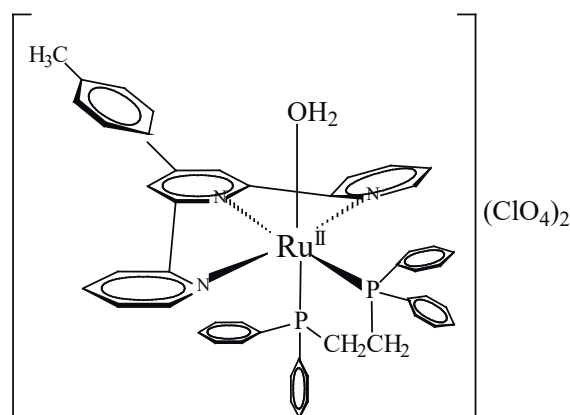
INTRODUCTION

The chemistry of metal complexes has received much attention due to their application as catalysts in important industrial processes (WANG *et al.*, 2019), and specially in processes developed according to the principles of Green Chemistry (SONG; ZHOU; HE, 2017).

In particular, ruthenium complexes have been used in several processes as, for example, catalytic hydrogenation (VAN RAVENSTEIJN *et al.*, 2017), transformation of amines in nitriles (CRISTIAN *et al.*, 2013). It is worthy to note that some ruthenium complexes have been successfully used in solar cells (AMETA; AMETA, 2016; AGHAZADA; NAZEERUDDIN, 2018); In medical research, some studies have shown that ruthenium (II) complexes are useful as a new generation of antitumor drugs (LIN *et al.*, 2018), since they exhibit higher efficiency and lower toxicity when compared to the platinum complexes that are commonly used (ABID; SHAMSI; AZAM, 2016; THOTA *et al.*, 2018).

Aqua polypyridyl complexes are an important class of compounds, and their electrochemical oxidation can produce high oxidation states in ruthenium complexes containing oxo ligands, which are exceptionally reactive sites for multi-electronic oxidation of substrates. We have studied catalytic systems using aqua complexes of ruthenium in a systematic way by varying the ancilliary ligands. We have found that ruthenium aqua/oxo complexes containing polypyridines, arsines or phosphines are more selective oxidants than those containing only polypyridines (LIMA *et al.*, 1998; SUSSUCHI; LIMA; DE GIOVANI, 2006; BATALINI; DE GIOVANI, 2020). On the other hand, metal complexes containing bidentate ligands, as diphosphine, are more stable than their monodentate analogues (CHAUDRET; DELAVAUX; POILBLANC, 1988; GAO *et al.*, 1996). In addition, tripyridine ligands in the coordination sphere increase the complex stability (MEYER, 1984; TSE *et al.*, 2005; EZHILARASU *et al.*, 2017).

We describe in this work the results obtained in the electrocatalytic oxidation of benzyl alcohol, benzaldehyde, benzylbutyl ether and 1-phenylethanol, in homogeneous aqueous phase, using a new ruthenium aquacomplex containing tripyridine and a bidentate diphosphine as ligands (Figure 1): $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)_2$ ($\text{L} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$); (*totpy* = 4'-(4-tolyl)-2,2':6',2''-tripyridine). As mentioned above, reaction processes in aqueous medium are clean, non pollutant and cheaper than those in organic solvents medium.

Figure 1 - Structure of $[\text{Ru}(\text{L})(\text{totpy})(\text{OH}_2)](\text{ClO}_4)$ ($\text{L}=\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$); ($\text{totpy}=4'-(4\text{-tolyl})-2,2':6',2''\text{-terpyridine}$).

Source: The author.

MATERIAL AND METHODS

Reagents and Solvents

Water was distilled twice from alkaline potassium permanganate (MORITA; ASSUMPÇÃO, 2007). Diethyl ether was previously dried by keeping it over anhydrous MgSO_4 , distilled and subsequently dried over metallic sodium and redistilled (MORITA; ASSUMPÇÃO, 2007). Methylene chloride was dried in an alumina column. All the other reagents and solvents, from Merck, Aldrich, Mallinckrodt and Sigma, were PA grade and used without further purification. The pH 8.1 solution was 7:3 phosphate buffer ($\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4 \cdot \text{H}_2\text{O}$) ($\mu=0.25 \text{ mol.L}^{-1}$):tert-butyl alcohol); the pH values were determined from direct pH meter readings and are therefore apparent pH values.

Instrumentation and measurements

Electrochemical experiments were carried out in a FAC-200 A potentiostat/galvanostat coupled to an Intralab current data logger. The bulky electrolyses experiments were performed in a two-compartment cylindrical cell using a platinum gauze working electrode (164.00 cm^2 , wire diameter of 0.16 mm), a platinum plate auxiliary electrode (1.00 cm^2 , thickness 0.20 cm) and a saturated calomel electrode (SCE). ^1H NMR spectra were recorded in a Bruker AC-80 (80MHz) NMR spectrometer, using deuterated chloroform as solvent and tetramethylsilane as internal standard (0 ppm on the δ scale). The GL chromatograms were obtained with a Varian 3400 chromatograph, equipped with a flame ionization detector, 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 length and 3.00 mm diameter.

General Procedure for the Electrooxidations

Electrochemical experiments were performed at room temperature and pressure in 7:3 phosphate:tert-butanol buffer solution, pH 8.1. The concentration ratios of the aqua ruthenium complex to the substrates were 1.00 mmol.L⁻¹ to 50.00 mmol.L⁻¹ respectively. The electrolyses were carried out at a fixed applied potential of +1.00 V (versus SCE); this potential is sufficient to generate the Ru^{IV}=O²⁺ oxidant from the correspondent Ru^{II}-OH₂²⁺ complex; the organic substrates were added and the electrolyses were continued until the current fell to about residual values or upon reaching the desired number of coulombs. The solutions were adjusted to approximately pH 10 by adding sodium hydroxide 1.00 mol.L⁻¹; the products of the electrolyses were extracted with diethyl ether (five extractions of 5 mL). In cases when benzoic acid should be identified, the remaining aqueous phases were acidified with concentrated hydrochloric acid to about pH 2.0, and extracted with diethyl ether. The products were analysed by gas chromatography, using cyclohexanol as internal standard, or by melting point and/or ¹H NMR.

Synthesis of the complex [Ru(L)(totpy)(OH₂)](ClO₄)₂ (L=Ph₂PCH₂CH₂PPh₂) (totpy=4'-(4-tolyl)-2,2':6',2''-terpyridine)

The synthesis of the complex [Ru(L)(totpy)(OH₂)](ClO₄)₂, involved three steps which is described in the literature (BATALINI; DE GIOVANI, 2023).

RESULTS AND DISCUSSION

The results of the electrocatalytic oxidations of organic substrates are summarized in Table 1.

Table 1- Electrocatalytic oxidations of organic substrates by [Ru(L)(totpy)(OH₂)](ClO₄)₂ (L=Ph₂PCH₂CH₂PPh₂); (totpy=4'-(4-tolyl)-2,2':6':2''-terpyridine) ^a.

Substrate ^b	I _i / I _r (mA)	Reaction Time (h)	% Applied charge	Product (s)	Yield (%) ^c
benzyl alcohol	8/2	20	100 ^d	benzaldehyde	43
benzaldehyde	8.5/2	16	100 ^d	benzoic acid ^f	51
benzylbutyl ether	14/3.8	29	100 ^e	benzaldehyde	10
				benzoic acid ^f	18
1-phenylethanol	14/6	8.5	100 ^e	acetophenone	86

^a 7:3 phosphate buffer:tert-butyl alcohol solution, pH 8.1. Catalyst concentration 1.00 mmol.L⁻¹.

Applied potential (vs. SCE): +1.00 V.

^b Substrate concentration 50.00 mmol.L⁻¹

^c Based on total coulombs passed.

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

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

^f Melting point obtained: 119-121°C (literature: 121-122 °C); ¹H RMN (d, CDCl₃): 12.0 (s, 1H); 8.20-8.10 (m, 2H) and 7.60-7.50 (m, 3H).

The results in Table 1 indicate that the reactions are selective generating only one product. This selectivity is particularly evident for oxidation of benzyl alcohol and 1-phenylethanol, when benzoic acid is not generated. The selectivity seems to occur by controlling the number of coulombs passed along with substrate concentration. Note that, in same reaction condition, benzaldehyde is oxidized to benzoic acid.

Table 2 shows electrocatalytic oxidations data obtained under same experimental conditions showed in Table 1 but in absence of the catalyst, to verify if the substrates could be oxidized by the electrode in the applied potential. The data reveal the important role of the aqua/oxo complex system in the electron transfer processes.

Table 2- Electrocatalytic oxidations of organic substrates in absence of [Ru(L)(totpy)(OH₂)](ClO₄).
(L=Ph₂PCH₂CH₂PPh₂), (totpy=4'-(4-tolyl)-2,2':6':2''-terpyridine) ^a.

Substrate ^b	I _i / I _f (mA)	Reaction Time (h)	% Applied charge ^c	Product	Yield (%) ^d
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 7:3 phosphate buffer:tert-butyl alcohol solution, pH 8.1. Applied potential (vs. SCE): +1.00 V.

^b Substrate concentration 50.00 mmol.L⁻¹

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

^d Based on total coulombs passed.

^e Melting point obtained: 119-121°C (literature: 121-122°C); ¹H RMN (d, CDCl₃): 12.0 (s, 1H); 8.20-8.10 (m, 2H) and 7.60-7.50 (m, 3H).

CONCLUSIONS

The results obtained in this work reveal the importance of using metallic complexes in electrocatalytic systems for transformation of organic compounds. In addition one can obtain high selectivity, with very good yields, in reactions using this catalyst class. It is worthy to note that beyond the mentioned advantages, the reactions are conducted in aqueous medium, in relatively short time, indicating that these processes are accomplished according to the principles of Green Chemistry.

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