

Electrocatalytic oxidation of alcohols and diols using polypyridyl complexes of ruthenium. Effect of the redox potential on selectivity

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Abstract

1-pentanol, 1,4-butanediol, 1,2-butanediol, 4-methoxybenzyl alcohol and phthalic alcohol were oxidized electrocatalytically by polypyridyl complexes of ruthenium in aqueous media. $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$, $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{py}(\text{OH}_2)]^{2+}$ (py = pyridine), $[\text{Ru}^{\text{II}}(\text{tpy})(\text{phen})(\text{OH}_2)]^{2+}$ (phen = 1,10-phenanthroline), *cis*- $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{OH}_2)]^{2+}$, *trans*- $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{OH}_2)]^{2+}$ and *trans*- $[\text{Ru}^{\text{VI}}(\text{tpy})(\text{O})_2(\text{OH}_2)]^{2+}$ were the studied complexes. A relationship between redox potential ($E_{1/2}$) of the complexes and reactivity was established. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polypyridyl oxo complexes of ruthenium can act as oxidants for a variety of organic functional groups [1–22]. A number of mechanistic pathways have been identified for these reagents, including O-atom transfer to sulfides [19], electrophilic attack on phenols [9], hydride transfer from alcohols [7,11,17] and proton-coupled electron transfer with hydroquinones [18]. For the $\text{Ru}^{\text{IV}}=\text{O}$ complex, the active center oxidizes the substrate and is reduced to the aqua species, $\text{Ru}^{\text{II}}-\text{OH}_2$. The Ru(IV) complex can be regen-

erated at a platinum electrode at a suitable positive potential. In this way, the complex can be used in catalytic amounts and recovered at the end of the process. For oxidation of C–H bonds, it is suggested that an electron-deficient carbon is formed in the transition state which can be attacked by water. In this sense, primary carbon can be oxidized to alcohol, then to aldehyde and then to carboxylic acid, in successive processes where two electrons, four electrons or six electrons are involved.

In particular, the complex $[\text{Ru}^{\text{IV}}(\text{tpy})(\text{bpy})(\text{O})]^{2+}$ (tpy = 2,2':6',2''-terpyridine; bpy = 2,2'-bipyridine) has been used in a systematic study, to oxidize electrocatalytically several classes of substrates: olefines [23], arenes [24], methyl-

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pyridines and their oxides [25] were oxidized to ketones and carboxylic acids; allyl and vinyl ethers yielded the corresponding esters [26], aliphatic and aromatic alcohols were oxidized to aldehydes and carboxylic acids [27]; diols gave rise to ketones and lactones [28]. The remarkable feature of the oxidation processes is that one can obtain very good selectivity by changing the experimental conditions [26–28] such as pH, number of coulombs and temperature.

We describe in this work the results obtained in the electrocatalytic oxidation of alcohols and diols using several polypyridyl ruthenium complexes. We compare the reactivities of the complexes as a function of their redox potential and oxidation state of the metal. The complexes were $[\text{Ru}^{\text{II}}(\text{tpy})(\text{bpy})(\text{OH}_2)]^{2+}$ (**1**), $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{py}(\text{OH}_2)]^{2+}$ (**2**) (py = pyridine), $[\text{Ru}^{\text{II}}(\text{tpy})(\text{phen})(\text{OH}_2)]^{2+}$ (**3**) (phen = 1,10-phenanthroline), *cis*- $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$ (**4**), *trans*- $[\text{Ru}^{\text{II}}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$ (**5**) and *trans*- $[\text{Ru}^{\text{VI}}(\text{tpy})(\text{O})_2(\text{OH}_2)]^{2+}$ (**6**). The substrates chosen for this study were: 1-pentanol, 1,2-butanediol, 1,4-butanediol, 4-methoxybenzyl alcohol and phthalic alcohol. Depending on the redox potential of the complexes, different yields were obtained for each substrate.

2. Experimental

2.1. Materials

Water was doubly distilled from alkaline potassium permanganate. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 2,2'-bipyridine, 2,2':6',2''-terpyridine, 1,10-phenanthroline, trifluoromethanesulfonic acid, hexafluorophosphoric acid, CDCl_3 , from Aldrich, perchloric acid EM Reagents, were used without further purification. Phthalic alcohol was prepared using a literature procedure [29] and characterized by ^1H NMR and IR spectra. All other solvents and chemicals were reagent grade or better and were used as received.

2.2. Preparations

The complexes: $[\text{Ru}(\text{tpy})(\text{bpy})(\text{OH}_2)](\text{ClO}_4)_2$ (**1**) [2,30], $[\text{Ru}(\text{bpy})_2\text{py}(\text{OH}_2)](\text{ClO}_4)_2$ (**2**) [31], $[\text{Ru}(\text{tpy})(\text{phen})(\text{OH}_2)](\text{ClO}_4)_2$ (**3**) [32], *cis*- $[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2](\text{PF}_6)_2$ (**4**) [33], *trans*- $[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2](\text{CF}_3\text{SO}_3)_2$ (**5**) [34,35] and *trans*- $[\text{Ru}(\text{tpy})(\text{O})_2(\text{OH}_2)](\text{ClO}_4)_2$ (**6**) [36,37], were prepared according to literature procedure.

2.3. Measurements

Routine UV–visible spectra were obtained in quartz cells by using a 634-S Varian or 8452A Hewlett-Packard spectrophotometer. IR spectra were recorded on a 1480 Perkin-Elmer spectrophotometer with nujol mulls or liquid films. ^1H NMR spectra were obtained in CDCl_3 solutions with a Bruker AC-80 spectrometer. GC chromatograms were recorded with Varian 3400 gas chromatograph. Electrochemical experiments were conducted by using a PAR model 273A Potentiostat/Galvanostat. Cyclic voltammetric experiments were conducted in a 10 ml one-compartment cylindrical cell using platinum working electrode (0.020 cm^2), a platinum wire auxiliary electrode and a saturated calomel reference electrode (SCE). The $E_{1/2}$ values for reversible couples were calculated from half the difference between E_p values for the cathodic and anodic waves. The bulky electrolyses experiments were performed in a 50 ml two-compartment cylindrical cell, at $25 \pm 1^\circ\text{C}$, using a platinum gauze working electrode (164 cm^2), a platinum plate auxiliary electrode (1 cm^2) and a SCE. The electrolyses were performed at fixed applied potential of $+0.80\text{ V}$ or $+1.12\text{ V}$ which are sufficient to generate $\text{Ru}^{\text{IV}}=\text{O}^{2+}$ or $\text{Ru}^{\text{VI}}=(\text{O})_2^{2+}$ oxidants from the corresponding aqua complex. The electrolyses were continued until the current fell to about residual values or upon reaching the desired number of coulombs. The substrates were unreactive under the experimental conditions, i.e., under potential of $+0.8\text{ V}$ or $+1.12\text{ V}$ the currents are in the microam-

Table 1
 $E_{1/2}$ potentials and UV–visible spectral data for the complexes in aqueous buffered solutions

Complexes	pH	$E_{1/2}$ (V)				λ_{\max} , nm ($\epsilon_{\max} \times 10^{-3}$, mol $^{-1}$ l cm $^{-1}$) ^{a,b}
		Ru ^{III/II}	Ru ^{IV/III}	Ru ^{V/IV}	Ru ^{VI/V}	
[Ru ^{II} (tpy)(bpy)(OH ₂)] ²⁺	6.8 ^c	+0.49	+0.62			477(9.418), 315 (32.440), 290(33.487), 280(31.394), 270(30.086), 230(27.365)
	7.0 ^d	+0.49	+0.62			318, 292, 276, 236; [III, +0.55 V]
	7.0 ^e	+0.48	+0.57			311, 287, 232; [IV, +0.80 V]
[Ru ^{II} (bpy) ₂ py(OH ₂)] ²⁺	6.8 ^c	+0.42	+0.53			470(8.372), 333(10.963), 290(55.816), 244(24.918)
	7.0 ^e	+0.42	+0.53			356, 290, 250; [III, +0.45 V] 290, 250; [IV, +0.80 V]
[Ru ^{II} (tpy)(phen)(OH ₂)] ²⁺	6.8 ^c	+0.49	+0.62			473(10.220), 316(34.268), 265(57.865), 230(47.345)
	7.0 ^f	+0.48	+0.58			365, 312, 265, 227; [III, +0.55 V] 316, 270, 227; [IV, +0.80 V]
<i>cis</i> -[Ru ^{II} (bpy) ₂ (OH ₂) ₂] ²⁺	4.5 ^c	+0.48	+0.71	+0.93	+1.06	488(8.894), 344(8.358), 290(65.366), 244(27.325)
	1.0 ^g	+0.65	+0.90	+1.10	+1.26	363, 300, 250; [III, +0.55 V]
	1.0 ^h	+0.64	+0.94	+1.12	+1.23	488, 300, 247; [IV, +0.80 V] 488, 300, 245; [V, +1.00 V]
<i>trans</i> -[Ru ^{II} (bpy) ₂ (OH ₂) ₂] ²⁺	4.5 ⁱ	+0.24	+0.72	(Ru ^{VI/IV} = +0.85)		488(12.120), 344(7.730), 290(50.200), 244(27.050)
	1.0 ^g	+0.44	+0.88	(Ru ^{VI/IV} = +1.01)		393, 356, 303, 256; [III, +0.75 V] 450, 303, 244; [IV, +0.85 V]
<i>trans</i> -[Ru ^{VI} (tpy)(O) ₂ (OH ₂)] ²⁺	4.5 ^j	+0.25	+0.62	(Ru ^{VI/IV} = +0.81)		414(3.910), 318(13.215), 284(15.250), 276(16.953), 264(17.744)
	4.0 ^k	+0.35	+0.64	(Ru ^{VI/IV} = +0.86)		

^aThis work; ϵ values are shown for the synthesized species; the other species were electrochemically generated.

^bThis work; The numbers between brackets represent the applied potential (volts) to obtain the corresponding species by exhaustive electrolysis (cardinal) and the formal oxidation number of the metal in species (ordinal).

^cThis work; platinum working electrode; scan rate 20 mV s $^{-1}$.

^dRef. [30].

^eRef. [31].

^fRef. [32].

^gRef. [35].

^hRef. [14].

ⁱThis work; platinum working electrode; scan rate 50 mV s $^{-1}$.

^jThis work; activated glassy-carbon working electrode; scan rate 100 mV s $^{-1}$.

^kRef. [37].

pere range. The products were extracted with Et₂O and identified by conventional methods. The pH of aqueous solutions were maintained by using perchloric acid, hexafluorophosphoric acid or trifluoromethanesulfonic acid (pH 1.0, $\mu = 0.1 \text{ mol l}^{-1}$), NaH₂PO₄ · H₂O (pH 4.5, $\mu = 0.5 \text{ mol l}^{-1}$), and NaH₂PO₄ · H₂O/Na₂HPO₄ · 2H₂O (pH 6.8, $\mu = 0.5 \text{ mol l}^{-1}$).

3. Results and discussion

The redox couples and the spectral data in aqueous solution for all studied complexes are presented in Table 1. Cyclic voltammograms of the complexes at pH 6.8 or 4.5 showed enhancement of the oxidation current in the presence of all studied substrates indicative of catalytic activities for all complexes. Fig. 1 shows, as examples, the cyclic voltammograms of all complexes in the presence of phthalic alcohol.

The compounds 1-pentanol, 1,2-butanediol, 1,4-butanediol, 4-methoxybenzyl alcohol and phthalic alcohol were electrolyzed in the presence of the ruthenium catalysts. The electrooxidations were conducted at controlled potentials of +0.80 V for the complexes **2** and **3** and +1.12 V for the complexes **4**, **5** and **6**. Attempts to conduct electrooxidation at +0.80 V and +0.70 V, respectively, using complexes **4** and **6** were unsuccessful. The low reactivity of **4** can be due to the proximity of oxo and aquo ligands in the *cis* position, inducing an intramolecular rearrangement with migration of hydrogen (H⁺/e⁻), originating the hydroxo–hydroxo complex which has lower reactivity [38]. A pH 4.5 aqueous solution of **6**, after controlled-potential electrolysis at +0.68 V, to obtain the Ru(IV) complex, *trans*-[Ru^{IV}(tpy)(O)(H₂O)₂]²⁺, shows an absorption band at 690 nm, which is characteristic of the μ -oxo dimer species [39]; the oxo-bridged dimer can become competitive with substrate oxidation and this can be responsible for the observed low reactivity.

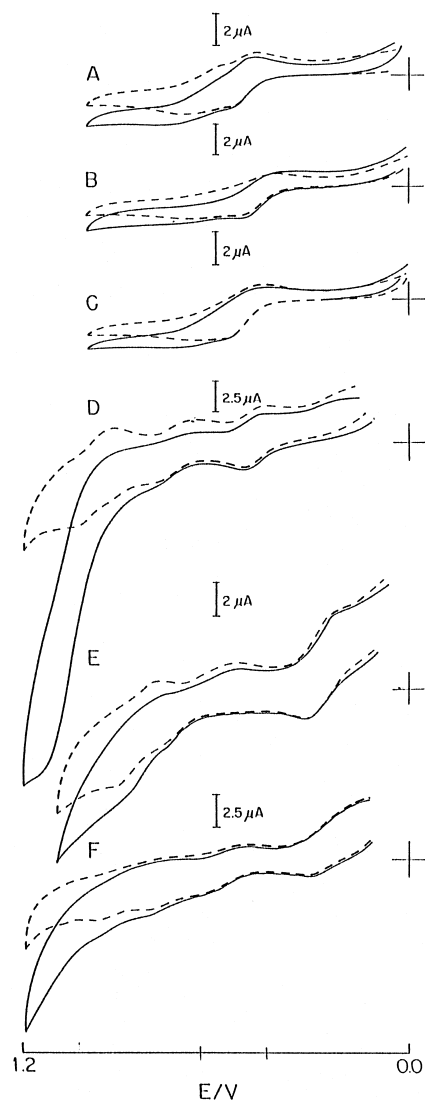


Fig. 1. Cyclic voltammograms at platinum electrode (diameter 3 mm) of the complexes (concentration = 1 mmol l⁻¹) in the absence (—) and in presence (---) of phthalic alcohol in phosphate buffer solutions; $\nu = 50 \text{ mV s}^{-1}$; [substrate] = 20 mmol l⁻¹, except for (B): 60 mmol l⁻¹. pH 6.8: (A) [Ru(tpy)(bpy)(OH₂)₂]²⁺, (B) [Ru(bpy)₂py(OH₂)₂]²⁺, (C) [Ru(tpy)(phen)(OH₂)₂]²⁺. pH 4.5: (D) *cis*-[Ru(bpy)₂(OH₂)₂]²⁺, (E) *trans*-[Ru(bpy)₂(OH₂)₂]²⁺, (F) *trans*-[Ru(tpy)(O)₂(OH₂)₂]²⁺.

The results of the electrocatalytic oxidations are summarized in Table 2. The following discussion about reactivities is based on the relation between yields of the products and the time of the electrolyses. In this case, it is assumed that the rate determining step is the substrate

Table 2
Electrocatalytic oxidation of alcohols and diols by using ruthenium complexes^a

Substrate ^b	Oxidative coulombs passed (complexes)						Reaction time (h) (complexes)						Products	Yields (%) ^c (complexes)					
	(1) ^d	(2) ^d	(3) ^d	(4) ^e	(5) ^e	(6) ^e	(1)	(2)	(3)	(4)	(5)	(6)		(1)	(2)	(3)	(4)	(5)	(6)
1-pentanol	401	–	384	418	474	407	26	–	23	22	23	08	1-pentanal	41	–	43	72	78	81
1,4-butanediol	651	–	380	381	533	777	20	–	25	27	22	23	γ -butyrolactone	44	–	25	58	53	83
1,2-butanediol	607	248	430	567	350	585	19	18	23	25	21	24	1-hydroxy-2-butanone	46	11	13	51	35	78
4-methoxybenzyl alcohol	190	370	270	390	350	512	04	05	20	27	09	2.5	4-methoxybenzaldehyde	35	22	71	30	53	65
4-methoxybenzyl alcohol ^f	330	308	175	346	332	436	03	06	16	27	20	04	4-methoxybenzoic acid	15	51	09	20	28	16
													4-methoxybenzaldehyde	77	33	39	41	45	55
phthalic alcohol	762	795	652	660	730	661	19	2.5	18	19	14	07	4-methoxybenzoic acid	15	18	06	13	07	10
													phthalic aldehyde	24	37	25	19	46	55
													phthalide	27	22	40	67	47	31
													3-hydroxyphthalide	10	19	13	10	–	07
phthalic alcohol ^g	660	493	615	658	663	625	22	18	19	22	14	18	phthalic acid	28	18	07	–	–	04
													phthalic aldehyde	30	45	29	35	38	38
													phthalide	54	30	58	46	40	43
													3-hydroxyphthalide	07	–	06	03	–	02
													phthalic acid	05	–	–	–	–	02

^aCatalyst concentration 3.12 mmol l⁻¹, unless otherwise noted.

^bSubstrate concentration 48 mmol l⁻¹.

^cBased on the amount of oxidized substrate, calculated from the number of coulombs passed.

^dpH 6.8.

^epH 4.5.

^fCatalyst concentration 1.56 mmol l⁻¹.

^gCatalyst concentration 0.78 mmol l⁻¹.

oxidation, with the assumption that the heterogeneous rates of re-oxidation of the complexes at the electrode is much faster than the chemical reaction. In this sense, it is neglected the different kinetic difficulties for different complexes that exist at the electrodes because of the combined electron–proton transfer mechanisms. The complex **2** which has the lowest redox potential (for the Ru^{IV}/Ru^{III} couple) is the least reactive, showing low reactivity with the aliphatic alcohols; it shows good selectivity in the oxidation of phthalic alcohol and, surprisingly, low reactivity in the oxidation of 4-methoxybenzyl alcohol. The complex **3** has the same redox potential than **1** but it is less reactive and more selective than the latter: it is worthy to note the high yield obtained in the selective oxidation of 4-methoxybenzyl alcohol and the very good selectivity in the oxidation of phthalic alcohol (when low concentration of the complex was used). The complex **4** which has the highest redox potential (for the Ru^{VI}/Ru^V couple),

showed the highest yield in the oxidations of aliphatic alcohols and, surprisingly, very good yield in phthalide in the oxidation of phthalic alcohol, using high concentration of the complex (it should be noted that there is a slow decomposition of the complex during the electrolysis, with loss of bipyridine ligand). Using complex **5**, good yields in phthalic aldehyde and phthalide, in oxidation of phthalic alcohol were obtained; another interesting point in this oxidation is the absence of 3-hydroxyphthalide and phthalic acid as products. The best yields in oxidations of monoalcohols were obtained using complex **6**, as well the best selectivities in oxidations of 4-methoxybenzyl alcohol and phthalic alcohol. The good reactivity of this complex can be due, probably, to its small volume making more effective contact with substrates.

Fig. 2 shows the correlation between reactivities and $E_{1/2}$ of the complexes. A generalization can be made: the benzyl alcohols are more reactive than the primary aliphatic alcohols; diol

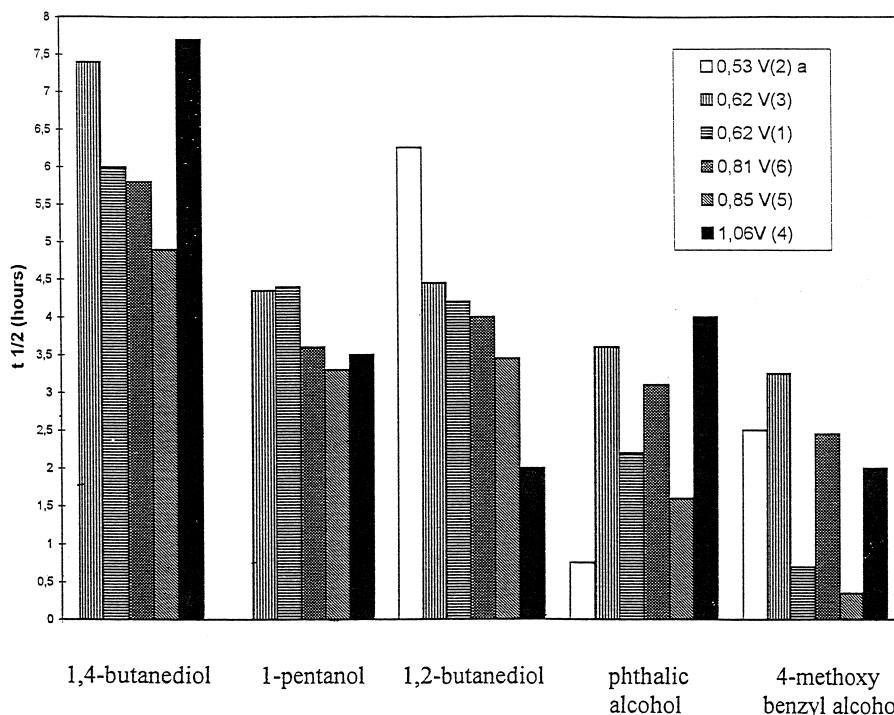


Fig. 2. Plot of half-lives ($t_{1/2}$) of the electrocatalytic oxidations. $t_{1/2}$ values were calculated from exponential regression of the experimental i vs. t curves [23]. ^aThe number in parenthesis represents the complex; the potential corresponds to the highest $E_{1/2}$ value.

containing secondary hydroxyl has an intermediate reactivity. It is observed that the reactivity decreases with the $E_{1/2}$ values in the oxidations of 1,4-butanediol, 1-pentanol and 1,2-butanediol; no reactivity order is observed in oxidations of 4-methoxybenzyl alcohol and phthalic alcohol. The complex **2**, which has the lowest $E_{1/2}$ value, is unreactive with 1,4-butanediol and 1-pentanol. Although the complexes **3** and **1** have the same $E_{1/2}$ value, the former is less reactive; this can be attributed to hindering for effective contact with the substrates, due to its larger volume. The more reactive complex (**4**) has the highest $E_{1/2}$ value.

4. Conclusions

The same products were obtained in oxidations of corresponding substrates for all studied complexes but with different yields for different complexes.

There is a direct relation between redox potential and reactivity of the complexes: higher $E_{1/2}$, higher reactivity.

The complex $[\text{Ru}(\text{tpy})(\text{phen})(\text{OH}_2)]^{2+}$ (**3**) containing the bulky ligand phen is the least reactive and showed highest selectivity in reactions with some substrates.

The best results, under the point of view of synthesis, were obtained with the complex $\text{trans-}[\text{Ru}^{\text{VI}}(\text{tpy})(\text{O})_2(\text{OH}_2)]^{2+}$ (**6**), which has high redox potential and relatively high stability compared to other complexes. Other interesting results: in the oxidation of phthalic alcohol using the complex $\text{trans-}[\text{Ru}(\text{bpy})_2(\text{OH}_2)_2]^{2+}$ (**5**) equal yields of phthalic aldehyde (46%) and of phthalide (47%) were obtained; using the complex $[\text{Ru}(\text{tpy})(\text{phen})(\text{OH}_2)]^{2+}$ (**3**), the oxidation of 4-methoxybenzyl alcohol yields 4-methoxybenzaldehyde (71%) and the oxidation of phthalic alcohol yields phthalide (58%); as already observed for (**1**) [28], the secondary hydroxyl group of 1,2-butanediol was selectively oxidized by all oxidant, instead of the primary one.

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