Electrocatalytic oxidation of alcohols, diols and arenes with ceric *p*-methoxybenzenesulfonate and ceric *p*-toluenesulfonate

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Abstract

The cerous *p*-methoxybenzenesulfonate (I) and cerous *p*-toluenesulfonate (II) mediators were prepared and studied by electrochemical and kinetic methods. The reactivity of several alcohols, diols and arenes in the oxidation reaction with I and II was established, and electrochemical oxidation of some of them was carried out, leading to products with selectivity. The behaviour of these mediators is in agreement with the results of the experiments, and can be explained by the effects produced by the different ligands. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Cerium ammonium hexanitrate (CAN) and cerium ammonium sulfate (CAS), in addition to other cerium salts, have been extensively studied as organic compound oxidants [1–7]. The high molecular weight of these salts, however, imposes technical difficulties on their use in preparative methods. Catalytic processes were developed using some slight redox co-reagent as chemical mediator [8–10].

Electrochemical methods using cerium salts as mediator have been applied to arene oxidation. Electrocatalytic oxidation of toluene to benzaldehyde with several cerium salts is a well known procedure [11–

13]. Using PbO_2 as anode, *p*-xylene was oxidized to *p*-tolualdehyde [11] and *p*-phenoxytoluene to *p*-phenoxybenzaldehyde [14–16] with CAS at 80°. Cerium methanesulfonate and cerium trifluoromethanesulfonate were studied in the electrocatalytic oxidation of alkylbenzenes and polynuclear aromatics [17–19].

Alcohol and diol oxidation by Ce^{IV} was not extensively studied in a preparative way. Ce^{IV} chemical oxidation of alcohols is largely dependent on structural effects [3,4]. Morita et al. immobilized cerium salts on a Nafion film to perform electrocatalytic oxidation of benzylic alcohols to their corresponding aldehydes [20,21].

Recently, we have investigated the electrocatalytic oxidation of a wide range of organic compounds using Ce^{IV} salts as electrochemical mediators [22–25]. When Ce^{III} nitrate [22] and Ce^{III} methanesulfonate [23–25] are anodically oxidized to Ce^{IV},

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they can perform one-electron oxidation of various organic substrates. These salts can convert alcohols and diols to aldehydes, ketones and carboxylic acids. They can also convert β-dicarbonylic compounds to fragmentation products with concomitant loss of $-CH_2-$ [23,25]. This occurs in a cyclic process where the oxidant functions as a catalyst.

To continue the studies on the chemical and electrochemical properties of cerium compounds in our laboratories, we have synthesised four new derivatives: cerous *p*-hydroxybenzenesulfonate, cerous alyll ether *p*-benzenesulfonate, cerous *p*-methoxybenzenesulfonate (I), and cerous *p*-toluenesulfonate (II). The first compound exhibited some very complicated electrochemical properties (oxidation of the ligand yielding quinone species), which prevented its use as an electrochemical mediator. The second presented electropolymerisation of the allyl function and was studied as a film for modified electrodes [26]. Mediators I and II were studied in the electrochemical oxidation of several alcohols, diols and arenes.

We have proved elsewhere [27] that different ligands in ruthenium complexes used as electrochemical oxidants affect the oxidation potential of the Ru^{II}/Ru^{III} and Ru^{III}/Ru^{IV} pairs due to their inductive, mesomeric and stereo effects. Thus, the higher the oxidation potential, the more reactive and less selective are the ruthenium complexes towards the oxidation of several classes of organic substrates. In the present study, *p*-methoxy and *p*-methyl groups were both used as electron donors. However, the first has a stronger mesomeric effect, while the other has a weaker inductive effect. Thus, they can influence the oxidation potential of Ce^{III} in different ways.

The objective of the present study was to determine the influence of the different ligands of I and II on the reactivity of these salts electrooxidised to Ce^{IV}, as well as their application in a selective and preparative way, using electrochemical techniques and kinetic and physicochemical determinations.

2. Experimental

2.1. Equipment

The electrocatalytic oxidations were carried out in a 50-ml one-compartment cell. A platinum gauze (164 cm^2 surface area, 16 mm wire diameter) was used as the working electrode and a platinum wire inside a sintered glass tube was used as the auxiliary electrode. A saturated calomel electrode (SCE) was used as the reference electrode. A PAR 273 Potentiostat/Galvanostat coupled to an Electrochemical Analysis software Model 270 and a Potentiostat MQPG- 01 coupled to the program MGPQ were utilized in the experiments and the current was registered on an Intralab 2030 recorder.

Cyclic voltammetry experiments were carried out in a cell (10 ml) using vitreous carbon as the working electrode (3 mm diameter), a saturated calomel electrode (SCE) as the reference, and platinum wire as the auxiliary electrode. Scans were carried out from 0.0 to $+2.0$ V, at 50 mV s^{-1}.

Kinetic experiments were carried out with a U3000/Hitachi Spectrophotometer and a Peltier Temperature Control model HP89090A, using a 3.0-ml quartz cell at a constant temperature of 40°C. A HPUV/Kinet program was used to register the absorbance data corresponding to a 325-nm Ce^{IV} decay for I and a 315-nm Ce^{IV} decay for II, and for the speed constant calculations.

The digital pH meter used in the potentiometric experiments was a Quimis model Q400A.

2.2. Reagents

All reagents and solvents were of analytical grade and were purified when necessary. Some substrates were synthesised according to methods described in the literature.

2.3. Analysis

Gas–liquid chromatographies were performed with an Intralab 3300 chromatograph equipped with an OV-17 column, an ionisation flame detector and an Intralab 4290 recorder. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained with a Bruker AC-80 (80 MHz) spectrometer. Infrared (IR) absorption spectra were recorded in a Perkin-Elmer 1600 series FTIR spectrometer using KBr pellets.

2.4. Preparation of sodium p-methoxybenzenesulfonate

Anisole (50.0 g, 50.1 ml, 0.450 mol) was added to a round-bottomed flask and heated to 50°C. Con-

centrated H_2SO_4 (26.6 ml, 0.495 mol) was added dropwise and under vigorous stirring and the mixture was stirred for 2 h at 100°C. H_2O (20 ml) was added to the cooled solution and then a saturated $NaHCO_3$ solution was added up to pH 8.0. The mixture was saturated with solid NaCl and a white solid precipitated. This was filtered and dried. This product was sufficiently pure for the next procedure and yielded 61.3 g (58%). ^{1}H NMR D_2O, δ (ppm): 3.75 (3H, s); 4.7 (2H, s: 1H$_2$O); 6.95 (2H, d); 7.7 (2H, d). IR (KBr), ν (cm^{-1}): 3444 (broad); 2500 to 1500 (several small aromatic bands); 1234 (large) and 1050 (large).

2.5. Preparation of I and II CE^{III} salts

A concentrated aqueous solution (20 ml, 3.0 g, 0.013 mol) of sodium p-methoxybenzenesulfonate was introduced in a column containing 30 ml of Amberlite IR-120 resin activated with HCl 0.1 mol l^{-1}. After water elution, the acid solution that left the column reacted with a stirred suspension of $Ce_2(CO_3)_3 \cdot H_2O$ (2.0 g; 0.004 mol) in water (15 ml). p-Toluenesulfonic acid (commercially available, 2.0 g, 0.013 mol, with one hydration water molecule) dissolved in 5 ml of water was added to a stirred suspension of $Ce_2(CO_3)_3 \cdot H_2O$ (2.0 g; 0.004 mol) in water (15 ml). CO_2 production was observed in the two reactions. The resulting solutions were heated at 100° for 30 min and evaporated and the two products (white solid) obtained were washed with dry acetone to eliminate excess of the sulfonic acid. Cerium p-methoxybenzenesulfonate (I), 8.7 g (89.7% yield), and cerium p-toluenesulfonate (II), 2.8 g (86% yield), were obtained.

I: ^{1}H NMR D_2O, δ (ppm): 3.75 (3H, s); 4.7 (2H, s: 7H$_2$O); 6.95 (2H, d); 7,65 (2H, d). IR (KBr), ν (cm^{-1}): 3444 (broad); 2500 to 1500 (several small aromatic bands); 1256 (large) and 1051 (large).

II: ^{1}H NMR D_2O, δ (ppm): 2.3 (3H, s); 4.7 (2H, s: 2H$_2$O); 7.2 (2H, d); 7,6 (2H, d). IR (KBr), ν (cm^{-1}): 3443 (broad); 2500 to 1600 (several small aromatic bands); 1636 (medium); 1145 (large) and 1051 (large).

2.6. General method for substrate electrocatalytic oxidation

A 1.6 V (vs. SCE) constant potential was applied to an electrolytic cell containing an aqueous solution (30 ml) of p-toluenesulfonic acid or sulfuric acid (0.5 mol l^{-1}) and Ce^{III} p-toluenesulfonate or Ce^{III} p-methoxybenzenesulfonate (0.1 mol l^{-1}), respectively. The colourless solution became yellow during the application of the charge necessary for the oxidation of Ce^{III}/Ce^{IV} and then the potential was interrupted.

Each of the studied substrates, 2.0 mmol (66.7 mmol l^{-1}), was then added to the above solution and a 1.5- to 1.7-V potential was applied under magnetic stirring at 25°C or 40°C. The initial yellow solution became colourless after substrate addition. The potential was applied until the amount of current corresponding to 2, 4 or 6 F mol^{-1} was passed through the solution. In the last stage of this electrocatalytic oxidation, very low current values were obtained ($\sim$ 1 mA, around residual current values). The crude product was extracted with methylene chloride (for expected aldehydes or ketones) or diethyl ether (for carboxylic acid). The solution was dried with anhydrous Na_2SO_4 and evaporated. Gas chromatography was carried out for identification and quantification of the products. When carboxylic acids were obtained, they were extracted from the ether solution with saturated $NaHCO_3$ solution. The solution was then acidified with concentrated HCl, kept in the refrigerator for 1 h and the precipitate was filtered, dried and weighed. Product characterisation was carried out by conventional analysis and melting point determination.

2.7. Kinetic study of substrate oxidation by I and II

A fresh Ce^{IV} solution was prepared as above by applying a 1.6-V potential to I and II. Ceric concentrations were determined by interpolation of $\lambda_{max.}$ absorption (325 nm for I and 315 nm for II) values from a Ce^{IV} absorption vs. concentration standard curve. This curve was obtained by modification of the titration of ceric sulfate described in the literature [28]. Several concentrations of ceric salt solutions were potentiometrically titrated with a standard solution of ferrous ammonium sulfate. I and II yielded 82.2% and 92.4% of Ce^{IV}, respectively.

One milliliter of a 1×10^{-3} mol l^{-1} solution of I and II was added to the quartz cell and kept at 40°C, under stirring. One milliliter of a 1×10^{-1} mol l^{-1} solution of each substrate was quickly added through

a syringe needle dipped in the cell solution and the record of the Ce^{IV} absorbance decay was initiated at the same time. The registrations were performed at different time intervals until an absorbance band at 325 or 315 nm no more appeared. The first-order speed constants were calculated for each substrate.

2.8. Acid constant determination

Solutions of *p*-methoxybenzenesulfonic acid and *p*-toluenesulfonic acid were potentiometrically titrated at room temperature with a 0.099 mol l^{-1} NaOH solution and the K_a was determined. Their concentrations were 0.166 and 0.095 mol l^{-1} and their K_a was 31.6 and 37.1.

3. Results and discussion

The voltammograms shown in Figs. 1 and 2 present two irreversible oxidation discharges at 1.37 and 1.73 V for I and 1.47 and 1.78 V for II. The higher potential in both cases was attributed to the metal oxidation Ce^{III}/Ce^{IV}, by comparing these values to other oxidation potentials of cerium salts [22–24]. Mediator II presented a slightly higher oxidation potential than I. The lower potentials in both cases were attributed to the ligands [26].
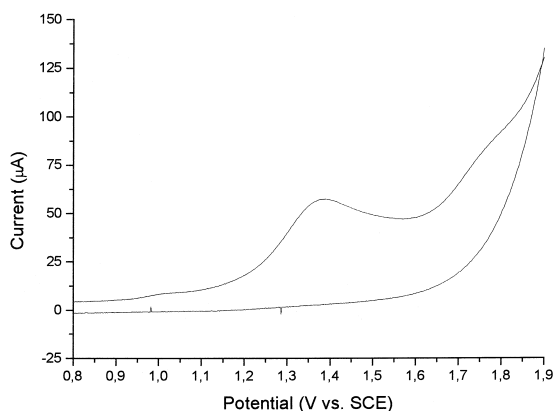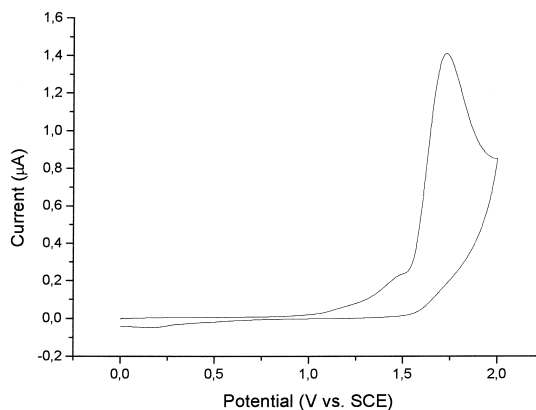
Fig. 2. Cyclic voltammogram for cerous *p*-toluenesulfonate (II) 0,05 mol l^{-1} in a *p*-toluenesulfonic acid 0.5 mol l^{-1} solution. Scan interval from 0.0 to +2.0 V and scan rate 25 mV s^{-1}.

The two mediators gave good yields of oxidised metal salts when a +1.6-V potential was exhaustively applied.

Table 1
First order (k_1, s^{-1}) speed constant for oxidation of the substrates mediated by I and II at +40°C

Substrate	I (k_1, s^{-1})	II (k_1, s^{-1})
Alcohols	Average: 1.17×10^{-3}	Average: 3.4×10^{-3}
Allyl	1.2×10^{-3}	1.2×10^{-3}
Benzyl	1.1×10^{-3}	1.2×10^{-3}
Cyclohexyl	1.6×10^{-3}	4.4×10^{-3}
Cyclopentyl	1.2×10^{-3}	2.8×10^{-2}
Propargyl	1.2×10^{-3}	1.7×10^{-3}
p-Methoxybenzyl	1.0×10^{-2}	2.2×10^{-2}
n-Pentyl	1.0×10^{-3}	7.8×10^{-3}
sec-Butyl	1.1×10^{-3}	6.1×10^{-3}
Diols	Average: 1.11×10^{-3}	Average: 3.35×10^{-3}
1,2-Butanediol	1.4×10^{-3}	9.2×10^{-4}
1,3-Butanediol	8.7×10^{-4}	2.1×10^{-3}
1,4-Butanediol	9.2×10^{-4}	3.2×10^{-3}
1,2-Cycloexanediol	8.5×10^{-4}	9.4×10^{-3}
1,3-Cycloexanediol	1.4×10^{-3}	1.0×10^{-3}
1,4-Cycloexanediol	9.5×10^{-4}	9.7×10^{-4}
Phthalyl alcohol	1.5×10^{-3}	5.2×10^{-3}
Arenes	Average: 1.2×10^{-3}	Average: 7.37×10^{-3}
Toluene	7.2×10^{-4}	9.0×10^{-3}
o-Xylene	9.5×10^{-4}	5.5×10^{-4}
m-Xylene	2.9×10^{-3}	2.1×10^{-2}
p-Xylene	1.2×10^{-3}	5.7×10^{-3}
Ethylbenzene	2.4×10^{-4}	6.3×10^{-4}

Fig. 1. Cyclic voltammogram for cerous *p*-methoxybenzene-sulfonate (I) 0.05 mol l^{-1} in a 0.5 mol l^{-1} H_2SO_4 solution. Scan interval from +0.8 to +1.9 V and scan rate 25 mV s^{-1}.

The kinetics of 20 substrate alcohols, diols and arenes with different structures were run, and a first-order speed constant for mediators I and II was calculated based on a 100-fold more concentrated solution of the substrates. We assumed, as shown in the oxidation mechanism studied for the ceric methanesulfonate salt [25], that the electron transfer from substrate to Ce^{IV} is the slower step. Table 1 shows that II is more reactive than I when one considers the average speed for the three substrate classes. This is noteworthy for the arenes. Comparison of each substrate in each class showed no significant difference in reactivity. Though not very reactive, both mediators could be used in electrocatalytic oxidation of some of the substrates studied.

Experiments 1 to 5 in Table 2 demonstrate that all of the chosen substrates reacted, yielding products. In some cases selectivity was achieved when different charges or potentials were applied. When benzyl alcohol was oxidised by II (experiment 1) with an applied potential of $+1.6$ V and an excess of $6e$ of charge, benzaldehyde was obtained in 63.6% yield and benzoic acid was obtained in 5.9% yield. By applying $+1.7$ V, with only $2e$ but closer than the oxidation potential of II (increasing its concentration in the reaction vessel), equivalent quantities of ben-

zaldehyde and benzoic acid were obtained. The higher the potential, the more one obtains of the most oxidised product benzoic acid. On the other hand, under the same conditions but using the less reactive (more selective) mediator I (experiment 4), a good yield of benzaldehyde (84.2%) was obtained and the product was not contaminated with benzoic acid.

In experiments 2 or 5, cyclohexyl alcohol was poorly oxidised to cyclohexanone (7.2% or 2.3% yield). But if one applies an excess charge ($8e$), this substrate gives adipic acid with 58.7% yield. This last result indicates that cyclohexanone is further oxidised in the α position until the cleavage of the ring occurs with an overall consumption of $8e$. A similar result was obtained when ceric methanesulfonate was used as mediator [24].

m-Xylene presented a low oxidation current at room temperature and therefore this substrate was studied at 40°C. Experiment 3 shows that only one methyl group was oxidised to give the three possible products, depending on the charge passed through the cell. With $6e$ and the more reactive mediator II, the main product was m-tolualdehyde (40.9% yield). m-Toluic acid was obtained in 3.4% yield. Similarly to the results presented for the benzyl alcohol oxida-

Table 2
Electrocatalytic oxidations of the chosen substrates with I and II

Experiment	Substrates	Mediator I and II		Products	Yield (%)	Faradaic yield (%)
1	Benzyl alcohol	II	$E_{appl.} = +1.5V\ (4e)$	benzaldehyde	28.5	24.9
			$E_{appl.} = +1.6V\ (6e)$	benzaldehyde	63.6	37.1
				benzoic acid	5.9	5.2
			$E_{appl.} = +1.7V\ (2e)$	benzaldehyde	13.1	14.3
				benzoic acid	13.0	14.2
2	Cyclohexyl alcohol	II, $E_{appl.} = +1.6$ V ($2e$)		cyclohexanone	7.2	6.9
3	m-Xylene[a]	II	$E_{appl.} = +1.6V\ (4e)$	m-methylbenzyl alcohol	10.9	4.7
				m-tolualdehyde	10.3	8.8
			$E_{appl.} = +1.6V\ (6e)$	m-methylbenzyl alcohol	24.9	11.9
				m-tolualdeyde	40.9	39.0
				m-toluic acid	3.4	4.9
		I	$E_{appl.} = +1.6V\ (6e)$	m-methylbenzyl alcohol	62.7	17.8
				m-tolualdeyde	2.2	0.9
				m-toluic acid	1.6	1.4
4	Benzyl alcohol	I, $E_{appl.} = +1.6$ V ($6e$)		benzaldehyde	84.2	49.1
5	Cyclohexyl alcohol	I, $E_{appl.} = +1.6$ V ($2e$)		cyclohexanone	2.3	2.0
		I, $E_{appl.} = +1.6$ V ($8e$)		adipic acid	58.7	55.4

[a] Reactions carried out at 40°C.

tion, when the less reactive mediator I ($6e$) was used, a good selectivity was achieved with a 62.7% yield of the less oxidised product *m*-methylbenzyl alcohol. The presence of the corresponding aldehyde and acid was negligible. A similar result had been previously obtained in our laboratory [29]. No other selective study with electrooxidation of organic substrate using cerium salts was found in literature.

These differences in reactivity in electrocatalytic oxidations, in addition to the differences in the oxidation potential, kinetic data and K_a determination, could be explained by the effect of the methyl and methoxy groups in the *para* position of the cerium salts. The mesomeric effect of the methoxy group increases the electron density of the sulfonic group or of the metal more than does the inductive effect of the far methyl group. The K_a determination of the corresponding acids showed that *p*-toluenesulfonic acid (37.1) is more acid than *p*-methoxybenzenesulfonic acid (31.6), similarly to the corresponding carboxylic acids [30]. The mesomeric effect on the sulfonic group makes it more highly negative (an effect transmitted to the metal in the salt) and thus less acid than does the inductive effect. The higher the electron density in the cerium, the smaller is the oxidation potential. Hence, the ceric *p*-methoxy-benzenosulfonate is less reactive and more selective while the ceric *p*-toluenesulfonate is more reactive and less selective.

4. Conclusion

The mediator ceric *p*-toluenesulfonate is slightly more reactive than the ceric *p*-methoxybenzenesulfonate in the oxidation of several alcohols, diols and arenes. The difference of reactivity is, therefore, sufficient to yield some products with interesting and useful selectivity using electrocatalytic oxidation process.

Acknowledgements

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