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Electrooxidation of Hydroxyl Compounds Using Cerium Salts as Mediators: The Importance of Substrate Size for Catalyst Regeneration

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The kinetics of a large series of smaller alcohols and diols and bulkier terpenol molecules was studied spectroscopically in order to determine the mechanistic importance of substrate size in the rate of electrocatalyzed indirect oxidation by Ce^{IV} mediators. Two mediators were used: Ce^{IV} *p*-toluenesulfonate (I) and *p*-methoxybenzenesulfonate (II), which lead to the fast formation of a Ce^{IV}–substrate complex. The next oxidation step was the slow and determinant step. The electronic effects were not important since the stoichiometry of the hydroxyl ligand and the sulfonic ligands was 1/6. The difference in reactivity was due to the larger size of the terpenols. It was demonstrated spectroscopically that a Ce^{III} complex is formed after the oxidation step and its size is important because it needs to be continuously reoxidized at the anode to continue the catalytic process. A higher reactivity of mediator II compared to mediator I was observed and it was possibly explained by the electronic effects of their ligands because they now have a 6/1 ratio of ligands vis-à-vis the hydroxyl ligand.

Key Words: **Ce^{IV} catalyst; Ce^{IV} mediator; electrocatalytic oxidation; Ce^{IV} *p*-toluenesulfonate; Ce^{IV} *p*-methoxybenzenesulfonate.**

INTRODUCTION

Among the lanthanides with a high oxidant power for organic substrates, cerium is the most useful for synthetic purposes, and several books (1–4) and reviews (5–8) about this subject are currently available. Cerium is the only lanthanide with a tetrapositive oxidation state sufficiently stable to coexist with organic ligands, and the cerium ammonium hexanitrate, $(NH_4)_2[Ce(NO_3)_6]$ (9), CAN, is the best known of its derivatives. Organic oxidation with ceric ion has been extensively studied (10–33), frequently with CAN, and the mechanistic postulation that has been made suggests a complex formation and the generation of a radical and/or cation radical in the organic intermediate (3, 4).

The use of CAN in organic synthesis is therefore limited due to its high molecular weight ($MW_{CAN} = 584$ g/mol) and its capacity to transfer only one electron. So, catalytic methods have been developed (34–37), such as electrocatalytic methods (15, 38–47), which require smaller amounts of mediators because they are continuously electrochemically oxidized.

Alcohols were oxidized by CAN or CAS (cerium ammonium hexasulfate) as catalyst and they can be regenerated by oxidants with lower molecular weights (20, 48–55) or by an electrochemical procedure (25–30). Several studies on the Ce^{IV} complex formation constants with alcohols or diols have postulated that the complex produced is 1 : 1, involving one molecule of the alcohol and one of the Ce^{IV} complex (56). This equilibrium is rapidly achieved, and, for many alcohols studied, the Ce^{IV}-alcohol complex produced is not sensitive to changes in the electronic nature of the hydroxyl group but the equilibrium constant increases when alcohols series becomes more sterically hindered (56, 57). Most results suggest a bidentate complex formation with the substrate (56).

A few kinetic studies of substrate oxidation are available in the literature but are limited to catalytic process. Carbonylic compounds such as ketones are rather interesting but their oxidation has been poorly explored with cerium reagents. Recently, Cho and co-workers (21–24) investigated the behavior of some β-dicarbonylic and β-cyanocarbonylic compounds in electrocatalytic oxidation using cerium reagents in acidic medium. Interesting results were attained when the products of the oxidation with cerous nitrate (21, 22) ($Ce(NO_3)_3$ anodically oxidized to Ce^{IV}) were compared with the products of the oxidation with cerous methanesulfonate (23, 24) ($Ce(CH_3SO_3)_3$ anodically oxidized to Ce^{IV}). In the first case only unsaturated dimers were obtained and in the second fragmentation products were obtained. The proposed mechanism suggests a bidentate ligand formation in the complex with cerium involving the enol structure of the β-dicarbonyl substrate where the oxygen of the carbonyl and hydroxyl groups form bonds with the metal (21–24). Also, complex formation is fast and the inner-sphere transfer of the first electron from substrate to Ce^{IV} is the slow and determinant step of the reaction. Air oxygen catalysis has also been reported (24).

Electrocatalytic oxidation of a series of alcohols with structural differences with Ce^{IV} *p*-toluenesulfonate and *p*-methoxybenzenesulfonates (25) showed a reduced

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influence of the electronic effects of the substrates. Some good results were attained when benzyl alcohol was oxidized to benzaldehyde (84.2% yield) or cyclohexyl alcohol to adipic acid (58.7% yield).

Concerning the relatively fast complex formation and the slow substrate oxidation, it is important to understand the kinetic features that influence the rate of oxidation when the process is catalytic and utilizes cerium salts as electrochemical mediators because the Ce^{III} formed needs to be continuously reoxidized at the anode for the process to go on.

We report here the spectroscopic and kinetic studies involving alcohol oxidation by Ce^{IV} *p*-toluenesulfonate (I) and *p*-methoxybenzenesulfonate (II) (25) using bulkier terpenol molecules and compare them with a large series of smaller alcohols and diols.

EXPERIMENTAL

Reagents

All reagents and solvents were of analytical grade and were purified when necessary. Some substrates were synthesized according to methods described in the literature. Substrates were alcohols and diols (25), reworked here under new experimental conditions, and terpenic alcohols (terpenols); all of them are listed in Table 1.

TABLE 1

Rate Constant k (s^{-1}) for Oxidation by Mediators I and II of Alcohols, Diols, and Terpenols

Substrate	Ce^{IV} *p*-toluenesulfonate	Ce^{IV} *p*-methoxybenzenesulfonate
Alcohols		
Benzyl	0.03	0.19
Sec-butyl	0.06	1.28
p-Methoxybenzyl	0.11	0.99
Cyclohexyl	0.12	0.74
Allyl	0.23	0.45
Cyclopentyl	0.09	0.87
n-Pentyl	0.58	1.57
Propargyl	0.10	0.17
Diols		
1,2-Butanediol	0.23	1.35
1,3-Butanediol	0.00067	0.03
1,4-Butanediol	0.00056	0.14
1,2-Cycloexanediol	0.00087	0.04
1,3-Cycloexanediol	0.00071	0.09
1,4-Cycloexanediol	0.00061	0.04
Phthalyl alcohol	0.00016	0.11
Terpenols		
Carveol	1.36	2.19
Citronelol	2.34	2.82
Geraniol	0.70	1.50
Menthol	2.51	1.90
Nerol	0.72	1.43

Equipment

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 a platinum wire as the auxiliary electrode. Scans were carried out from 0.0 to +2.0 V, at 50 mV $\cdot$ s^{-1}.

The electrocatalytic oxidations were carried out in a 50-ml one-compartment cell. Platinum gauze (164-cm^2 surface area, 16-mm wire diameter) was used as the working electrode and 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 Potentiostat MQPG-01 coupled to the MGPQ program was utilized in the experiments and the current was registered on an Intralab 2030 recorder.

Kinetic experiments were carried out with an HP model 8453 Spectrophotometer and a Peltier Temperature Control model HP89090A, using a 3.0-ml quartz cell at a constant temperature of 40°C. An HPUV/Kinet program was used to register the absorbance data corresponding to a 325-nm Ce^{IV} decay for I and a 340-nm Ce^{IV} decay for II.

The Origin 5.0 software was used for graph presentation, for the exponential and linear regressions, and for the rate constants calculation. The CS Chem Draw and CS Chem 3D (58) programs were used to calculate the Van der Walls area for some substrates.

Analysis

Gas–liquid chromatographies were performed with an Intralab 3300 chromatograph equipped with an OV-17 column, an ionization 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 absorption spectra were recorded on a Perkin–Elmer 1600 series FTIR spectrometer using KBr pellets.

Preparation of I and II Oxidants

A constant 1.6-V (vs SCE) potential was applied to an electrolytic cell containing 50 ml of an aqueous/terc-butanol (1 : 1) solution of *p*-toluenesulfonic acid or sulfuric acid (0.25 mol $\cdot$ L^{-1}) and Ce^{III} *p*-toluenesulfonate (I) or Ce^{III} *p*-methoxybenzenesulfonate (II) (5×10^{-2} mol $\cdot$ L^{-1}). The colorless solution became yellow during the application of the charge necessary for the oxidation of Ce^{III} to Ce^{IV}. The applied potential was maintained during the kinetic experiments to assure the same concentration of Ce^{IV}.

Kinetic Study of Substrate Oxidation by I and II

A 1.0-ml aliquot of a 1×10^{-4} mol $\cdot$ L^{-1} solution of I and II prepared as above was added to the quartz cell and kept at 40°C under stirring. A 1.0-ml aliquot of a 1×10^{-2} mol $\cdot$ L^{-1} solution of each substrate (1 : 1 aqueous/terc-butanol) was quickly added through a syringe needle dipped into the cell solution and the record of the decay of Ce^{IV} absorbance was initiated at the same time. The registrations were performed at 0.5-s intervals until an absorbance band at 325 nm for I or 340 nm for II no longer appeared or remained stable. A first-order rate constant was calculated for each substrate (Table 1) based on absorbance data.

Electrocatalytic Oxidation of the Terpenol Substrates

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 $mol \cdot L^{-1}$) and Ce^{III} *p*-toluenesulfonate or Ce^{III} *p*-methoxybenzenesulfonate (0.1 $mol \cdot L^{-1}$). The colorless solution became yellow during the application of the charge necessary for the oxidation of $Ce^{III}$to $Ce^{IV}$and then the potential was interrupted. Each of the terpenol substrates, 2.0 mmol ($\approx$0.4 $mol \cdot L^{-1}$), was added to the above solution and a 1.5- to 1.7-V potential was applied under magnetic stirring at 40°C. The initial yellow solution first became red and then colorless after substrate addition. The potential was applied until the amount of current corresponding to 2, 4, or 6 $F \cdot mol^{-1}$ was passed through the solution. In the last stage of the electrocatalytic oxidation, very low current values were obtained ($\sim$1 mA, around residual current values). The crude product was extracted with diethyl ether and the solution was dried with anhydrous Na_2SO_4 and evaporated. Gas chromatography was carried out for identification and quantification of the products.

RESULTS AND DISCUSSION

Electrocatalytic Oxidation of the Terpenol Substrates

For all five terpenols studied, gas–liquid chromatography showed a yield of about 80% of the starting materials and several other products not isolated.

Kinetic Study of Substrate Oxidation by I and II

We present here the UV spectra for 1,2-butanediol and for citronelol (Figs. 1 and 2 for I and Figs. 3 and 4 for II, respectively) and the graphs of the reaction and exponential regression curves (Figs. 5 and 6 for I and Figs. 7 and 8 for II). Because it is impossible to present the spectra and graphs for all reactions, these substrates were chosen due to their good performance and representativity.

Regarding the UV spectra for I (Figs. 1 and 2) there was almost no absorption for the Ce^{III} oxidation state of the salt or when the substrate was added. Ce^{IV} absorption is difficult to see due to scale but there were strong absorptions between 280 and 310 nm when the substrate was added (formation of the Ce^{IV}–substrate complex) and an increase in the neighbor Ce^{IV} absorption at 325 nm was observed. After the decay of this Ce^{IV} absorption, absorptions in the

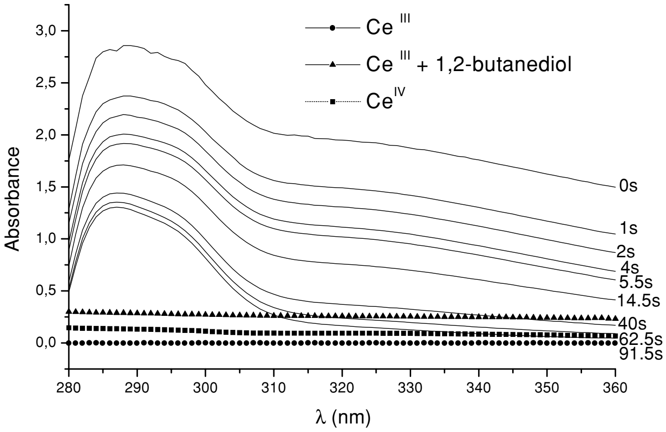

FIG. 1. UV–visible spectra of the reaction of 1,2-butanediol with mediator I.

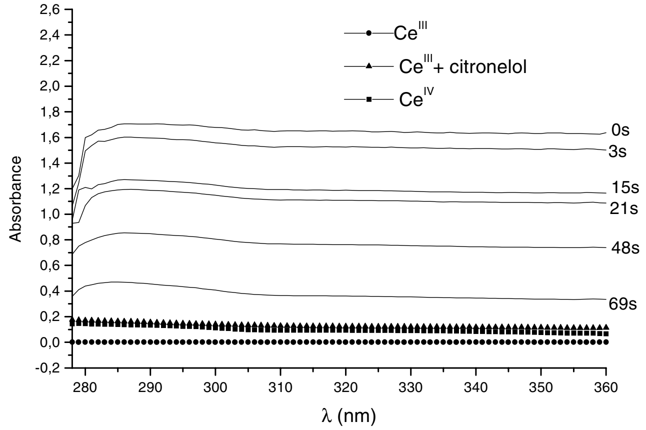

FIG. 2. UV–visible spectra of the reaction of citronelol with mediator I.

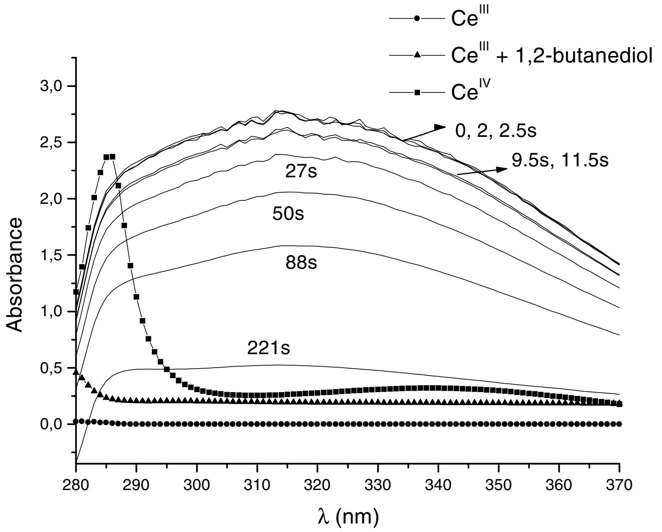

FIG. 3. UV–visible spectra of the reaction of 1,2-butanediol with mediator II.

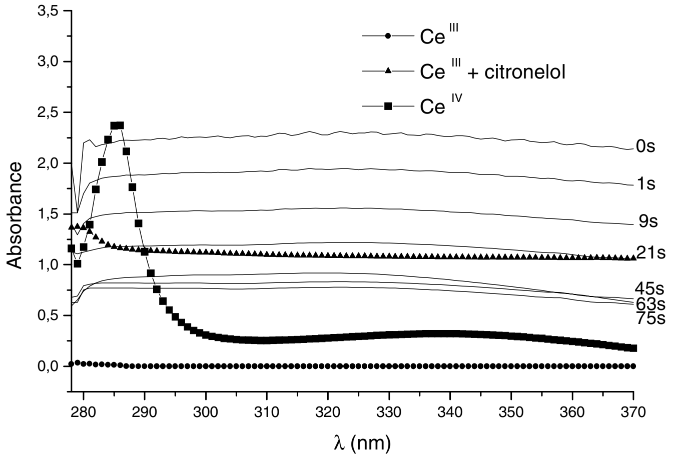

FIG. 4. UV–visible spectra of the reaction of citronelol with mediator II.

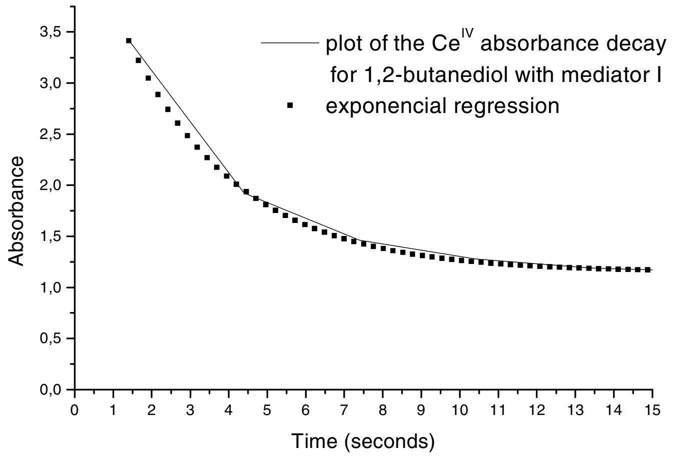

FIG. 5. 1,2-Butanediol oxidation with mediator I. Decay of the Ce^{IV} UV–visible absorption.

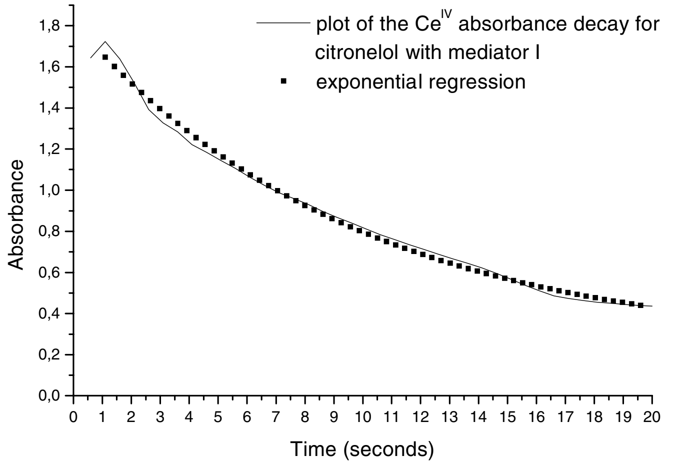

FIG. 6. Citronelol oxidation with mediator I. Decay of the Ce^{IV} UV–visible absorption.

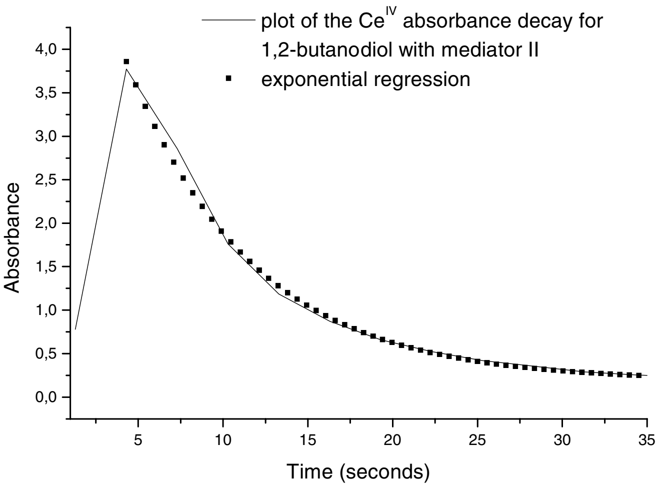

FIG. 7. 1,2-Butanediol oxidation with mediator II. Decay of the Ce^{IV} UV–visible absorption.

280- to 310-nm range (Ce^{III}–product complex) were observed. The same spectral characteristics can be seen for II (Figs. 3 and 4), plus an absorption that can be attributed to the *p*-methoxybenzenesulfonic ligand at 285 nm.

Figures 5–8 show a good coincidence of the experimental and exponential regression curves taken from the λ_{max} for the Ce^{IV} decay when they began after an initial growth (a few seconds) due to the formation of the Ce^{IV}–substrate complex.

All of the other 18 substrates presented similar behavior in these spectroscopic studies.

Mechanistic Proposition

As observed for the oxidation of β-dicarbonyl compounds with cerium methanesulfonate, UV–visible spectra

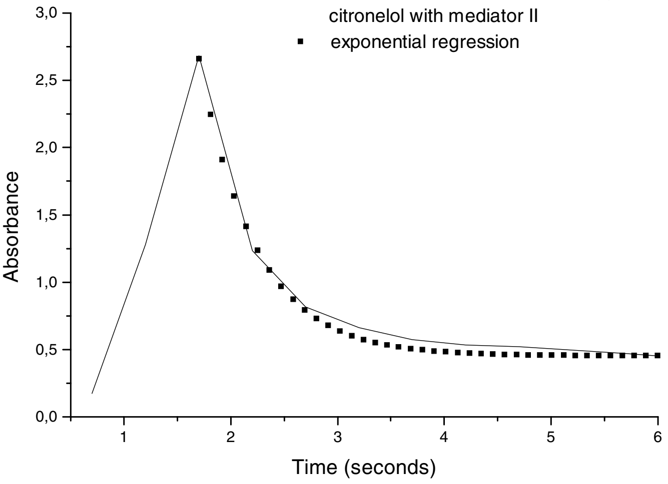

FIG. 8. Citronelol oxidation with mediator II. Decay of the Ce^{IV} UV–visible absorption.

showed that there was no product formation when these hydroxyl compounds were mixed with I or II when the metal was in the Ce^{III} oxidation state. Mediators I and II did not present significant UV–visible absorption besides those attributed to the normal ligand chromophore absorption. When oxidized to Ce^{IV}, intense absorptions occurred in the 280- to 300-nm range that could be attributed to complex formation with Ce^{IV}, in addition to those at 325 and 340 nm for I and II, respectively, characteristic of ligand → metal Ce^{IV} transition. All these Ce^{IV} mediator complexes proved to be stable in solution before the substrate addition (21–25) with no electron transfer from ligand to Ce^{IV} due to the high oxidation state of the sulfonic group of the mediator.

All of the substrates studied here presented several bands in the 280- and 310-nm range (ξ near 300 $\text{mol} \cdot \text{L}^{-1} \cdot \text{cm}^{-1}$); bands were reported for ceric methanesulfonate with β-dicarbonyl compounds, in the 200- to 300-nm range. These absorptions were attributed to the coordinated Ce^{IV}–substrate bond due to the displacement of one bond of the bidentate *p*-toluenesulfonic or *p*-methoxybenzenesulfonic by the hydroxyl substrate.

Although we did not monitor the kinetics of complex formation, we observed that the corresponding bands appeared during at least the first 5 s before the addition of the substrate to the mediator in the cell, together with the change in the characteristic yellow color of Ce^{IV} to red. Ce^{IV}absorption initially increases similarly fast and then decays exponentially at a remarkably slower rate than the formation of the complex. Considering that the concentration of the substrate is 10^2 times higher than that of the oxidant, some influence on the rate due to the position of the complex equilibrium (an increase in the equilibrium constant caused by an increase in the steric hindrance of the alcohol) can be minimized. So, the substrate oxidation step is the slow and determinant step. The graph for Ce^{IV}-to-Ce^{III} decay was plotted immediately after the initial absorbance increase. After the decay due to Ce^{IV} reduction to Ce^{III}, the 280- to 310-nm absorptions continued to be present even with some modifications, indicating that once the complex is formed it remains also in the Ce^{III} oxidation state. This fact is important because we focus here on the effect of the substrate size (now as a complex with cerium) and the necessity of its electrochemical reoxidation for the mediator to perform efficiently as a catalyst.

The rate of this reaction, which corresponds to the first electron transfer from substrate to metal, was consider as first order (we took into account these relative values) because, according to the proposed mechanism, the electron transfer is inner sphere, which depends exclusively on the concentration of the complex species. The graph plotting of the corresponding equation was compatible with the results and good correlation coefficients close to unit were obtained for almost all substrates studied.

Table 1 shows, in general, no noticeable variation in rate constant for each substrate class. One can reaffirm here that electronic effects are not important. It is appropriate to consider that only one molecule of hydroxyl cannot modify substantially the chemical properties of a complex that has six other ligands. An increase in the rate constant occurred when we changed mediator I to II and an important increase in terpenol rate constant occurred with both mediators. The less reactive class of substrate was diol, except in the case of 1,2-butanodiol, which had a 10^3 times higher rate constant, and the terpenols were the most reactive. A close evaluation of the relative reactivities with mediator I shows that alcohols are 10^3 times more reactive than diols and terpenols are 10^5 times more reactive. With mediator II, alcohols are 10 times more reactive than diols and the terpenols are 10^2 times more reactive, or 10^5 if compared with diols oxidized by I. Note that also here 1,2-butanodiol was the more reactive ($\approx 10^2$ times) compared with the other diols.

The noticeable difference in reactivity is due to the bigger size of the terpenols. The Van der Walls surface (Å^2) of terpenols compared with other two chosen alcohols is citronelol, 98.67; carveol, 93.13; mentol, 95.93; geraniol, 85.97; nerol, 85.93; benzyl alcohol, 68.63; and cyclohexyl alcohol, 62.91 (58). We then propose the mechanism illustrated in Fig. 9, showing the total oxidation of a primary hydroxyl substrate to aldehyde (involving two electrons and loss of two H^+) or carboxylic acid ($-2e$, $-2H^+$), as previously obtained (25). As described by the authors for the equilibrium formation of a complex with CAN (56), one of the bidentate ligands (here the sulfonic group) is displaced by the hydroxyl molecule (fast step). We describe it as following the slow oxidation step (electron transfer from substrate to Ce^{IV} with the decay of absorption), producing the oxidized Ce^{III}–alcohol complex with the loss of H^+ and the subsequent anodic reoxidation of this complex to Ce^{IV}. This electron transfer we postulate to be an inner-sphere transfer. In the quartz cell reaction, where the kinetic experiments were studied, only the first step occurs because the oxidant is less concentrated than the substrate, but with the *in situ* constant-current generation of Ce^{IV}, the oxidation of aldehydes to carboxylic acids can take place.

The geometry of the Ce^{IV}complex is octahedral bipyramidal and, as we have proposed for ceric methanesulfonate in comparison with ceric nitrate (23, 24), six acid *p*-toluenesulfonic or *p*-metoxybenzenesulfonic ligand molecules are bound in a bidentate fashion, giving a coordination number equal to 12 (Fig. 9) and an icosahedral distorted stereochemistry (59). When $Ce^{IV}$is reduced to Ce^{III}, a cerous anion with a coordination number 10 is produced (59). Although the charge passes from +4 to +3, a sterical decompression is expected by the loss of one ligand that favors the accommodation of the other ligands. So, the oxidation of the substrate by the reduction of cerium leads to a

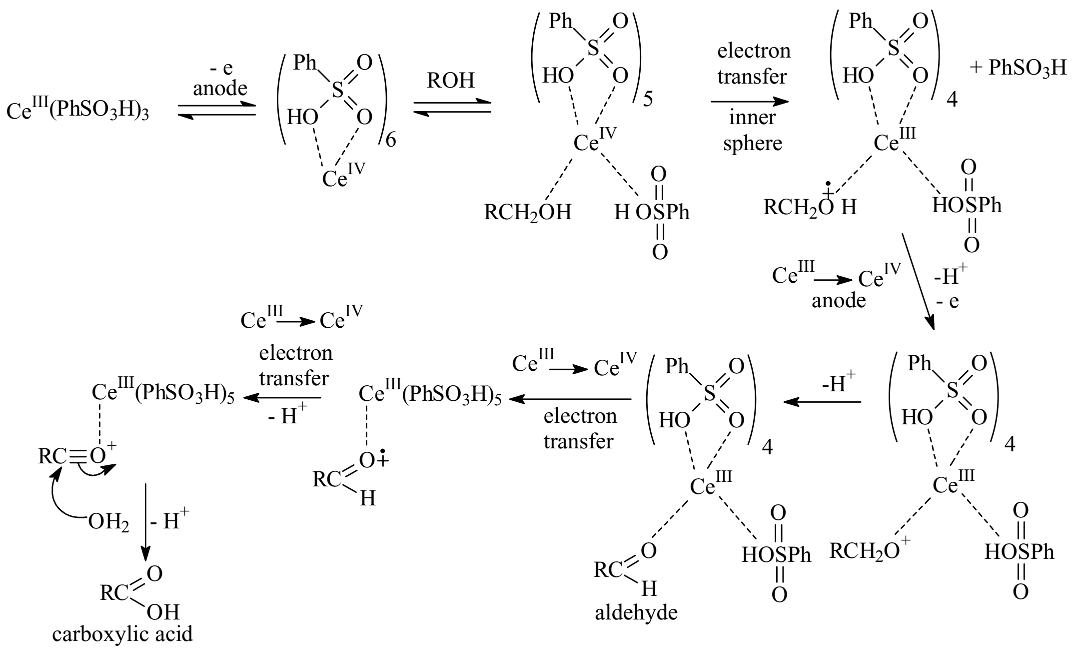

FIG. 9. Mechanistic proposition for oxidation of a hydroxyl substrate by a Ce^{IV} mediator.

reduction in the size of the complex. Complex formation is an equilibrium rapidly attained and a nondeterminant step for the reaction as a whole, but it supplies material continuously for the next low and determinant electron transfer step. The substrate oxidation will be faster as the volume of the ligand increases.

The fact that we can observe a Ce^{III}-oxidized substrate complex explains the difficulty of the anodic reoxidation: two phases (solution and electrode) are present in this process in which the size of the electroactive species is crucial. Generally the rate of this cerium sulfonate electrocatalytic oxidation is not fast and will be slower when the substrate is bulkier. In this way, electrocatalytic oxidation produced good results with alcohol but failed completely with the terpenols, yielding a small amount of several unidentified products, probably derived from the Ce^{III} complex decomposition.

1,2-Butanodiol proved to be more reactive than its homologues because it probably yielded a bidentate complex displacing one molecule of the sulfonic ligand. The other diols had no adequate sterical characteristic to yield a bidentate complex. The presence of two hydroxyl oxygen bound to cerium increases the probability of the electron transfer from substrate to Ce^{IV}.

An attempt to explain the greater reactivity of mediator II could be proposed due to the electronic effects of its ligands that, now, with a 6/1 stoichiometry vis-à-vis the hydroxyl ligands, can cause a perceptible difference in rate. The greater +R effect of the *para* methoxy group compared with the +I of the *para* methyl group further increased the electronic density of the II sulfonic group that became stronger coordinatively bound to Ce^{IV}, with shorter bonds. Thus, the inner-sphere electron transfer from hydroxyl ligands to the close metal became easier and more rapid.

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