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RESEARCH NOTE

Oxygen as an Oxidizing Agent in Electrocatalytic Oxidation of β-Dicarbonylic Compounds Using Ce^{IV} as a Mediator

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Oxygen from air improves the ceric methane sulfonate-mediated electrochemical oxidation of 2,4-pentanedione, 1,3-cyclohexanedione, 1,3-diphenyl-1,3-propanedione, diethyl malonate, and ethyl acetoacetate, giving fragmentation products. An increase in the yield and decrease in the time required for these transformations with no changes in the products or in the electron stoichiometry allow us to propose a mechanism where the oxygen oxidizes an intermediate complex formed between the substrate and the mediator, in a fast step. A dioxygen radical intermediate formed in the process is anodically reduced. © **2000 Academic Press**

Key Words: **oxygen as an oxidizing agent; β-dicarbonyl compounds; ceric methanesulfonate; electrooxidation; oxidative fragmentation.**

INTRODUCTION

We have investigated the electrocatalytic oxidation of a wide range of organic compounds using Ce^{IV} salts as electrochemical mediators (1–3). When Ce^{III} nitrate and Ce^{III} methane sulfonate are anodically oxidized to Ce^{IV}, they can perform one-electron oxidation of various organic substrates. Re-oxidized to Ce^{IV}, these salts can convert alcohols and diols to aldehydes, ketones, and carboxylic acids, in a cyclic process where the oxidant functions as a catalyst.

β-Dicarbonylic compounds such as 2,4-pentanedione (**I**), 1,3-cyclohexanedione (**II**), 1,3-diphenyl-1,3-propanedione (**III**), diethyl malonate (**IV**), and ethyl acetoacetate (**V**) can be electrocatalytically oxidized by the Ce^{III} methane sulfonate mediator, generating fragmentation products with concomitant loss of $–CH_2–$ (2, 4). I renders acetic acid; II gives glutaric acid; III leads to benzoic acid; IV gives ethanol; and V generates acetic acid and ethanol. It has been possible to demonstrate that the methylene group present between the two carbonyl groups is oxidized to CO_2 (4).

Kinetic studies have shown that substrates **I**, **II**, and **III**, which are β-diketones, react faster than substrates **IV** and **V**, which are a β-diester and a β-ketoester, respectively. β-Dicyano and β-ketocyano derivatives such as malononitrile or ethyl cyanoacetate are inert in the presence of the Ce^{IV} mediator. Spectroscopic and coulometric studies have allowed the establishment of a mechanistic proposal where a complex is formed between the Ce^{IV} mediator and the enolic form of the β-diketone. Substrates **IV** and **V** are less reactive since they lead to little or no enol formation. Electron transfer from the substrate to the metal occurs through an inner-sphere process. The fact that CO_2 is detected as a product in the oxidation of **I** and that coulometric studies of all the electrocatalytic oxidations indicate the consumption of four electrons ($+H_2O$, $-4H^+$) have led us to suggest the formation of a 1,2,3-tricarbonylic intermediate in the reaction medium. Being unstable under the reaction conditions, this intermediate decomposes to the reaction products (4). By carrying out the reaction open to air, it has been possible to notice that it proceeds faster than the reaction performed under an inert atmosphere.

The aim of this work is therefore to show that oxygen favors these electrocatalytic oxidations by acting as an oxidizing agent in the electron transfer step, which has not yet been reported in the literature.

For this work, the electrocatalytic oxidations were carried out in three different ways: open to air (open system); under argon bubbling; and under air bubbling. The Ce^{III} methane sulfonate mediator was dissolved in a methane sulfonic acid solution. In the case of substrate **III**, which is insoluble in this medium, an acetonitrile/water mixture was used since the presence of water is necessary for the reaction to occur. Additionally, substrate **I** was carried out to react under pure oxygen bubbling too. The time required for the transfer of four electrons was measured in each case and the products were analyzed. The turnover of each reaction was also calculated. Both separation and purification

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procedures were the same for all the substrates used in this work.

METHODS

Equipment. The electrocatalytic oxidations were carried out in a 50-ml one-compartment cylindrical 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 employed as the auxiliary electrode. A saturated calomel electrode (SCE) was used as the reference electrode. A PAR 273 potentiostat/galvanostat was utilized in the experiments and the current was registered in an Intralab 2030 recorder. All the experiments were magnetically stirred at the same speed. In the experiments where the cell solution was saturated with either argon, air, or pure oxygen, the latter were bubbled through the cell with the aid of a Pasteur pipette, after being previously passed through a solution of the same composition as the one to be used throughout the reactions. Care was taken to maintain the gas flow approximately the same in all the experiments.

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.

Preparation of the Ce^{III} methane sulfonate mediator. This was prepared by adding methane sulfonic acid (6.32 g; 65.8 mmol) dropwise to a suspension of Ce^{III} carbonate (5.00 g; 10.9 mmol) in water (20 ml). The reaction mixture was stirred until no more CO_2 production was observed. The mixture was then filtered and the solvent was eliminated under vacuum, at 90°C. A white solid was obtained and washed with acetone (10 ml) to eliminate the excess acid. This solid (hygroscope) was dried until constant mass and then weighed (7.55 g; 8.17 mmol; 75% yield). ^{1}H NMR (D_2O), δ (ppm): 2.8 (3H, s), 4.7 (4H, s = corresponding to $2H_2O$). **IV**, KBr, ν (cm^{-1}): 3419 (w, broad), 1630 (m), 1198 (w), 1055 (w), 788 (m).

Oxidation of Ce^{III} methane sulfonate. A 1.6-V potential (vs SCE) was applied to an electrolytic cell containing 30 ml of a methane sulfonic acid (0.5 mol L^{-1}) and cerous methane sulfonate (0.05 mol L^{-1}) solution either in an open system, under argon bubbling, or under air or pure oxygen bubbling. This was done until the current had fallen to residual values (1 F mol^{-1}), after a few minutes. The same procedure was applied to an experiment where a water/acetonitrile mixture (4 and 26 ml, respectively) was used as a solvent. In a fifth experiment, the mixture was left to stir in the cell with no applied potential, either in the presence or in the absence of air bubbling, for 4 h. This was the time required for the stabilization of the absorbance band at 296 nm, assigned to the Ce^{IV} metal/ligand transition. UV–vis spectra of these experimental solutions were performed in the range of 200–280 nm and the absorption band due to the presence of Ce^{IV} was analyzed.

General method for substrate electrocatalytic oxidation. A 1.6-V (vs SCE) potential was applied to an electrolytic cell (open to air, under magnetic stirring at 25°C) containing an aqueous solution (30 ml) of methane sulfonic acid (0.5 mol L^{-1}) and Ce^{III} methane sulfonate (0.05 mol L^{-1}). The colorless solution became yellow. After the 145 C necessary for oxidation of Ce^{III}/Ce^{IV} was passed through the solution, the potential application was interrupted.

Two millimoles (66.7 mmol L^{-1}) of each of the studied substrates was then added to the previous solution and a 1.6-V (vs SCE) potential was applied under magnetic stirring at 25°C. The initial yellow solution became colorless upon substrate addition. The potential was applied until the amount of coulombs corresponding to 4 F mol^{-1} has been passed through the solution. In the last stage of this electrocatalytic oxidation, very low current values were obtained (~1 mA, around residual current values). The substrate concentration used in the case of **III** was half that used for the other substrates due to its lower solubility in the water/acetonitrile (1/6.5) reaction medium.

The same procedure was used when the reaction was performed under argon or air bubbling. The same experimental procedure was also used when the reactions were carried out either in an open system, under argon, or under air bubbling, but in a water/acetonitrile mixture.

2,4-Pentanedione (**I**) was also oxidized with pure oxygen bubbling following exactly the same procedure used previously.

The crude product was extracted with diethyl ether (50 ml) in a liquid–liquid extractor overnight. The solvent was dried with anhydrous Na_2SO_4 and evaporated and the product was weighed. In the experiments where substrates **I**, **IV**, and **V** were used, gas chromatography was carried out for identification and quantification of products. This was done by comparing the products' retention times and peak areas with those of solutions of known concentrations. When **II** or **III** were used, their respective carboxylic acids were extracted from the ether solution with saturated $NaHCO_3$ solution. The solution was then acidified with concentrated HCl and kept in the refrigerator for 1 h, and the precipitate was filtered, dried, and weighed. Product characterization was carried out by conventional analysis and melting point determination.

Analysis. Gas–liquid chromatographies were performed in an Intralab 3300 chromatograph equipped with an OV-17 column, an ionization flame detector, and an Intralab 4290 recorder.

UV–visible absorption spectra were recorded on an 8452A HP spectrophotometer. All the spectra were registered at 28°C.

TABLE 1

Reaction Time Required for the Electrochemical Oxidation (1.6 V vs SCE) of a CH_3SO_3H (0.5 mol L^{-1}) and $Ce(CH_3SO_3)_3$ (0.05 mol L^{-1}) Solution

	Reaction time (min)[a]	
Experience	Aqueous medium	Acetonitrile medium
Open system	30	30
Argon	36	35
Oxygen from air	16	24
Pure oxygen	19	—

[a] Necessary for 1 F mol^{-1}.

RESULTS AND DISCUSSION

Results presented in Table 1 show that there is a 47% reduction in the time required for the Ce^{III}/Ce^{IV} oxidation to occur when the direct electrochemical oxidation of the Ce^{III} methane sulfonate mediator is carried out in aqueous solution under air bubbling (a decrease of 37% occurs under pure oxygen bubbling). When oxygen is removed from the reaction medium through argon bubbling, the reaction time increases by 13%. The same behavior is observed when acetonitrile is used as the solvent, although to a lesser extent. In this solvent and in the presence of oxygen, the reaction time is decreased by 20% and it is increased by 16% when oxygen is removed.

Conductometric titration studies of Ce^{IV} solution by potassium ferrocianate (4, 6) have shown that the efficiency of the Ce^{III}/Ce^{IV} transformation in the electrooxidation carried out in an open system is 92% (UV–vis spectroscopy of the product: $\lambda_{max.} = 296$ nm; ξ, 1720 (mol $L^{-1})^{-1}$ cm^{-1}). If the mediator aqueous solution in its acid is left to stir without any applied potential, either in the presence (ξ,1300 (mol $L^{-1})^{-1}$ cm^{-1}) or in the absence (ξ, 1008 (mol $L^{-1})^{-1}$ cm^{-1}) of air bubbling, the Ce^{III}/Ce^{IV} oxidation efficiency is 75.6% in the former case and 58.6% in the latter case. These results are based on the absorbance of Ce^{IV} obtained in the electrooxidation carried out in an open system. The presence of an oxidant acid alone in solution can be partially responsible for the oxidation of Ce^{III}. The presence

TABLE 2

Products, Turnover, and Reaction Times of the Electrocatalytic Oxidation of Organic Substrates Using a CH_3SO_3H (0.5 mol L^{-1}) and $Ce(CH_3SO_3)_3$ (0.05 mol L^{-1}) Solution

Substrate (66.7 mmol L^{-1})	Reaction medium saturation	Product yield (%)	Turnover	Charge ($C = 4$ F mol^{-1}), Initial current (mA)	Reaction time (h)
		Acetic acid[a]			
2,4-Pentanedione (**I**), aqueous medium	Open system	86	4588	802–32	20
	Argon	84	4482	778–53	21
	Air	90	4800	799–61	4
	Pure oxygen	87	4640	800–360	2.9
		Glutaric acid[b]			
1,3-Cycloexanedione (**II**), aqueous medium	Open system	59	3148	771–20	26
	Argon	54	2881	773–35	28
	Air	62	3308	773–120	11
		Glutaric acid[b]			
1,3-Cycloexanedione (**II**), acetonitrile medium	Open system	34	1814	770–30	27
	Air	54	2881	766–78	13
		Benzoic acid[b]			
1,3-Diphenyl-1,3-propanedione (**III**), acetonitrile medium	Open system	65	1734	384–10	15
	Agron	50	1334	380–8	20
	Air	73	1947	383–17	8
		Ethanol[a]			
Ethyl malonate (**IV**), aqueous medium	Open system	77	4108	779–80	15
	Argon	84	4482	780–60	16
	Air	78	4162	796–82	2
		Acetic acid[a]			
Ethyl acetoacetate (**V**), aqueous medium	Open system	27	1440	777–80	8
	Argon	26	1387	777–80	15
	Air	85	4536	772–120	2.5
		ethanol[c]			

[a] Chromatographic yields.

[b] Yield of purified products.

[c] Variable yield but detect in each experiment.

of oxygen increases the efficiency of such a transformation. However, the oxidation is slow (4 h) and incomplete, if compared to the results obtained when Ce^{III} oxidation potential is applied to the cell (a few minutes).

Table 2 presents the results obtained in the electrocatalytic oxidations of the studied substrates, in aqueous solution, in three different ways: in an open system, under argon bubbling, and under air bubbling (also with pure oxygen bubbling for substrate **I**). To better understand the effect that replacing water for an acetonitrile/water solvent mixture in the case of substrate **III** may have in the reaction, we have also presented the electrocatalytic oxidation of substrate **II** in this latter medium.

One can observe that the products obtained with a given substrate are always the same. The turnover is dependent on the yield. Yields are higher in the presence of air and lower when it is not present. The increase in yield ranged from 1.3% (for substrate **IV**) to 215% (substrate **V**) in an aqueous medium, while in acetonitrile/water it ranged from 12.3% (substrate **III**) to 58.8% (substrate **II**). The charge that was passed through the solution was always 4 F mol^{-1} and the initial currents were always higher when there was air saturation. It is noteworthy that a 360-mA current was reached for the initial current when pure oxygen was used for **I**, instead of 61 mA in the case of air bubbling. The time required for the transformations were always higher in the absence of oxygen and noticeably lower in its presence. The variation was in the range of 2.4 (substrate **II**) to 7.5 (substrate **IV**) times in aqueous solution and 1.9 (substrate **II**) to 2.1 (substrate **III**) in acetonitrile/water. This difference between the two media may be explained by the higher solubility of oxygen in water. If pure oxygen was bubbled, as in the experiment with substrate **I**, the time required was 6.9 times faster than that in the open to air experiment (5 times faster than air bubbling).

So the efficiency of the reaction is better in the presence of oxygen when one takes into consideration both the total reaction times and yields. This increase in efficiency is much more pronounced than that in the case of the Ce^{III}/Ce^{IV} direct oxidation, indicating that oxygen acts directly in the electron transfer between substrate and mediator: the proposed mechanism for such oxidation postulates a complex formation between the substrate and the mediator, and it is the metal in this intermediate that is successively oxidized by the anode (4).

Another very important factor is that the number of coulombs required for the consumption of four electrons was not altered by more than 2.2% in all cases (4 F mol^{-1}). This means that oxygen took part in the reaction but did not alter the electron stoichiometry.

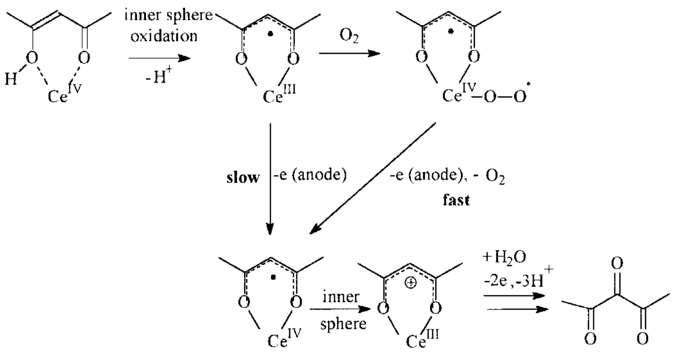

FIG. 1. Mechanistic proposition of oxygen as oxidizing agent.

The factors decrease in reaction time, obtainment of the same products, and no alteration in electron stoichiometry lead to the conclusion that oxygen catalyzes the electrooxidation of the studied β-dicarbonylic compounds mediated by Ce^{IV} methane sulfonate.

It is possible to propose a mechanism for oxygen participation in electrocatalysis as shown in Fig. 1, in the case of substrate **I**.

Oxygen present in the reaction solution oxidizes Ce^{III} to Ce^{IV} in the radical metal–substrate complex remaining as a dioxygen radical bound to the metal. Further, this intermediate is anodically oxidized to molecular oxygen in a fast step. Concomitantly, an anodic oxidation occurs, yielding the same Ce^{IV} radical, but in a slow step. This continues the process to give the tricarbonylic intermediate. The presence of oxygen in a faster competitive reaction increases the rate of the overall process and the electron stoichiometry is maintained. The faster oxidation of the radical dioxygen at +1.6 V is easily understood if one considers its similarity with superoxide, which has a low oxidation potential ($E_{1/2} = -0.41$ vs SCE) (7).

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