Journal of Catalysis **186,** 31–35 (1999)
Article ID jcat.1999.2541, available online at http://www.idealibrary.com on IDEAL®

Electrooxidation of β-Dicarbonyl Compounds Using Ceric Methanesulfonate as Mediator: Some Kinetics and Spectroscopic Studies

L. Y. Cho, J. M. Madurro, and J. R. Romero[1]

Dep. Química, FFCL, Rib. Preto, USP. Av. Bandeirantes, 3900, 14040-091, Ribeirão Preto, Sao Paulo, Brazil

Received October 8, 1998; revised April 28, 1999; accepted April 30, 1999

β-Dicarbonyl compounds 2,4-pentanedione (I), 1,3-cyclohexanedione (II), 1,3-diphenyl-1,3-propanedione (III), methyl acetoacetate (IV), dimethyl malonate (V), methyl cyanoacetate (VI), and malononitrile (VII) were submitted to electrocatalytic oxidation mediated by Ce^{IV} anodically generated from cerous methanesulfonate, $Ce(CH_3SO_3)_3$. I, II, III, IV, and V decompose yielding their respective carboxylic acids, methyl alcohol and CO_2, via a proposed tricarbonylic intermediate. Four electrons per mole are consumed in these reactions. VI and VII proved to be unreactive. The reactivity order found was I $\cong$ III > II > IV > V. The substrates that form larger quantities of enol in reaction medium (β-diketones) are the most reactive, followed by the β-ketoester that forms less enol and the diester that forms no enol. An enol–Ce^{IV} complex is formed and the electron transfer is postulated as being "inner sphere." © 1999 Academic Press

Key Words: **electrooxidation; β-dicarbonyl compounds; mediator; ceric methanesulfonate; oxidative fragmentation.**

INTRODUCTION

β-Dicarbonyl, β-cyanocarbonyl, and β-dicyano compounds containing active methylenes can be oxidized to yield interesting products (1–8). Chemical oxidation with cerium ammonium nitrate, CAN ($(NH_4)_2Ce(NO_3)_6$), or electrocatalytic oxidation with Ce^{IV} electrogenerated from cerous nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) was studied in our laboratories (5). With CAN, 2,4-pentanedione, methyl acetoacetate, and dimethyl malonate yielded saturated dimers, and methyl cyanoacetate yielded an unsaturated dimer. Mediated electrochemical oxidation produced unsaturated dimers with all of these substrates. Saturated dimers were formed by radical carbon bonding after $H^{\bullet}$ ($-e$, $-H^+$) abstraction from methylene and unsaturation was obtained by the subsequent oxidation of the methynes from these dimers (four electrons per mole of unsaturated product). The difference in reactivity was given by steric hindrance imposed to reagents by the substrates. CAN, more bulky than Ce^{IV} from cerous nitrate oxidation, proved to be unable to promote the second oxidation, except for methyl cyanoacetate, the smallest of the substrates.

Subsequently (6), 2,4-pentanedione (I), 1,3-cyclohexanedione (II), 1,3-diphenyl-1,3-propanedione (III), methyl acetoacetate (IV), dimethyl malonate (V), methyl cyanoacetate (VI), and malononitrile (VII) were submitted to electrocatalytic oxidation mediated by Ce^{IV} anodically formed from cerous methanesulfonate, $Ce(CH_3SO_3)_3$, (VIII) (9). In contrast to the previous compounds obtained (5), carbonyl substrates yielded fragmented structures with loss of "CH_2," i.e., acetic acid (90% yield), glutaric acid (75%), benzoic acid (61%), acetic acid (84%) plus methanol (undetermined yield), and only methanol (64%), respectively, for I to V. Nitrile substrates were unreactive.

In all of the above cases, reactive substrates led to development of a dark red color from a light yellow color, typical of the Ce^{IV} ion, immediately after the components of the reaction (CAN or the mediator with substrates) were mixed. This observation led us to postulate the formation of a substrate–Ce^{IV} complex. In this last study, dicarbonyl function is necessary for the reaction.

We present here a spectroscopic and kinetics study of the oxidation of the substrates I to V mediated by Ce^{IV} anodically formed from VIII and a mechanistic proposition for the fragmentation reaction.

METHODS AND RESULTS

The oxidations were carried out in cylindrical cells with a capacity of 60 mL, using a platinum gauze with an area of 164 cm^2 (diameter 0.16 mm) as the working electrode and a 1 cm^2 platinum wire, within a sintered glass tube as the auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). A Potentiostat/Galvanostat PAR model 273 was used and current was recorded with an Intralab Recorder model 2030.

UV-visible spectroscopy was carried out in a thermostated cell with an optical path of 1.0 cm in an HP 8452A or

---

[1] To whom correspondence should be addressed.

0021-9517/99 $30.00

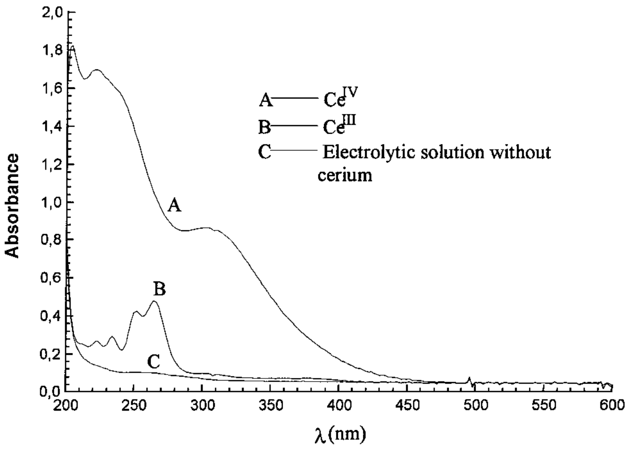

FIG. 1. UV-visible spectra for Ce^{III} and Ce^{IV} methanesulfonate salts.

Hitachi U3000 spectrophotometer. All measurements were made at 26°C.

Solvents were GC grade and reagents were commercial or synthesized in our laboratories.

Ceric Methanesulfonate Preparation

A potential of 1.5 V vs SCE was applied to an electrolytic cell containing 60 mL of a 0.5 mol L^{-1} methanesulfonic acid and $5 \cdot 10^{-2}$ mol L^{-1} VIII solution. After 289 coulombs necessary for the $Ce^{III} \rightarrow Ce^{IV}$ transformation, a yellow solution was obtained. UV-visible spectra of the Ce^{III} and Ce^{IV} solutions are presented in Fig. 1, which shows the $\lambda_{max} = 302$ nm absorption characteristic of the ligand → metal (Ce^{IV}) transition.

UV-Visible Spectroscopy

All substrates were analyzed by UV-visible spectroscopy in the reaction solution (0.5 mol L^{-1} methanesulfonate acid) in which the kinetics study was carried out. Dimethyl malonate, methyl cyanoacetate, and malononitrile were transparent, whereas the others have absorptions shown in Table 1.

TABLE 1

Absorption in UV-Visible Spectroscopy of I to IV Substrates

Substrate	Concentration mmol L^{-1}	λ_{max} nm (ξ(mol $L^{-1})^{-1}$ cm^{-1})
2,4-pentanedione	0.5	274 (1830)
1,3-cyclohexanedione	0.016	255 (18280)
methyl acetoacetate	0.5	256 (180)
1,3-diphenyl-1,3-propanedione[a]	0.019	251 (13930)[b] and 346 (19460)

[a] Solution containing 80% of acetonitrile, methanesulfonic acid 0.5 mol L^{-1}.

[b] Phenyl.

All of these absorptions, as well as that at 346 nm of 1,3-diphenyl-1,3-propanedione, were assigned to the enol function of the β-dicarbonyl compounds. The enol absorption intensities of the β-diketones were significantly stronger than that of the β-ketoester due to the smaller amount of the enol form in tautomeric equilibrium for this last substrate.

Coulometric Measurement of Substrate Electrooxidation

In an electrolytic cell, 2.0 or 3.0 mmoles of substrates I to VII were added to 30 mL of an aqueous solution of 0.5 mol L^{-1} methanesulfonic acid and 0.05 mol L^{-1} of mediator VIII, previously oxidized to Ce^{IV} by application of a potential of +1.5 V vs SCE (145 coulombs, 1 F/mol). Substrates I to IV changed the solution color from yellow to dark red. A potential of 1.5 V vs SCE was applied at 26°C with vigorous magnetic stirring. The red color (yellow for V) of the solutions disappeared after several seconds to give a transparent solution, except for substrates VI and VII, which maintained the yellow color. These latter substrates did not cause passage of any current. The others gave initial currents varying from 58 to 90 mA, and electrolyses were carried out until the current fell exponentially to residual values (≈1 mA). Products were extracted and analyzed according to procedures described in the literature (6). The number of coulombs was given by the coulometer of the potentiostat or measured by the integration of the recorded current vs time curve (no more than 10% difference). All of the substrates from I to V consumed a number of coulombs (approximately 778 C for 2.0 mmoles of substrate and 1180 C for 3.0 mmoles of substrate) that corresponds to 4 electrons/molecule and they presented turnover of 5.1, 4.0, 4.9, 4.5, and 5.1, respectively.

Detection of CO_2 as a Product of Electrooxidation of Substrate I

The total time for electrolysis was very long (6), with consequent difficulties in detecting gases as products of these electrooxidations. However, it was possible to detect qualitatively CO_2 for the particular oxidation of 2,4-pentanedione because this substrate was the most reactive and presented the highest initial current (90 mA). Two inlet and outlet devices were set up in the electrolytic cell. A small flow of argon was run through the cell and bubbled into a solution of barium hydroxide. Some minutes after the potential was applied, a white precipitate of barium carbonate was observed, denoting the formation of CO_2 in the reaction vessel.

Kinetics of Substrate Oxidations by Ce^{IV} Mediator

Substrates I to VII were initially studied by UV-visible spectroscopy in the 200 to 600 nm range (they were transparent above this value) at 26°C by addition of 0.5 mL of a 5.0 mmol L^{-1} solution of each substrate to 2.0 mL of a 0.5 mmol L^{-1} solution of VIII. These solutions were prepared from aqueous 0.5 mol L^{-1} methanesulfonate acid. For III, insoluble in this medium, it was necessary to utilize a solution with 80% acetonitrile, maintaining the same composition and concentration as for the other solutions. UV-visible spectra did not show any change in the previous absorptions due to the enol or Ce^{III} chromophore (Fig. 1). No complex or any other product was formed by reaction of the substrates with mediator VIII.

Forty mL of a solution containing 0.5 mol L^{-1} methanesulfonate and 0.5 mmol L^{-1} of VIII was then exhaustively oxidized by applying a potential of 1.5 V vs SCE and this potential was maintained while 2 mL aliquots were withdrawn. These portions were mixed with 0.2 mL of a 0.5 mol L^{-1} solution of methanesulfonic acid and with the substrate at a concentration of 5.0 mmol L^{-1}. Thus, the mixture contained a 1:1 ratio of oxidizing reagent and substrate and the dilution used did not matter because the concentrations were calculated by interpolation of the absorption from a standard curve. This mixture was added to the cell at 26°C in the spectrophotometer with rapid insertion of the substrate solution by means of a pipette, and the spectra were recorded immediately in the 200 to 600 nm range at 0.5 s intervals. A similar experiment was performed for substrate III in the 80% acetonitrile mixture as co-solvent in order to evaluate qualitatively its reactivity.

In this reaction mixture enol absorption was not more observed. Substrates I, II, III, and IV showed now important modifications in the intensity and appearance of the bands in the region from 200 to 280 nm (absorptions attributed to the interactions of the Ce^{IV} with the substrates) at the beginning of the reaction, but soon the spectra became identical with that of mediator VIII. Figure 2 shows the most apparent and expressive modification obtained with 1,3-cyclohexanedione (II). It can be seen that several very intense absorptions between 200 and 280 nm appeared during the first seven seconds of the reaction.

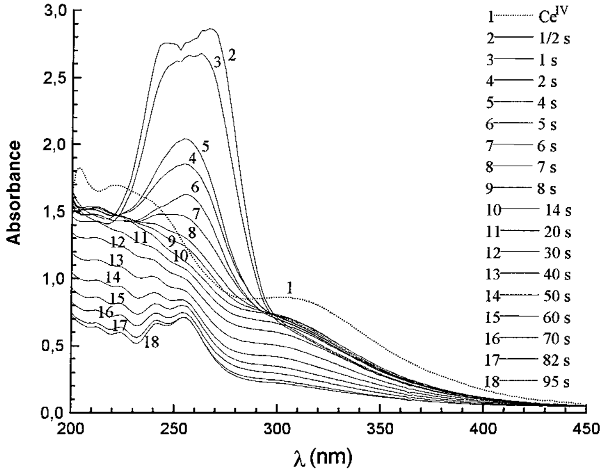

FIG. 2. UV-visible spectra of the reaction of 1,3-cycloexanedione with ceric methanesulfonate.

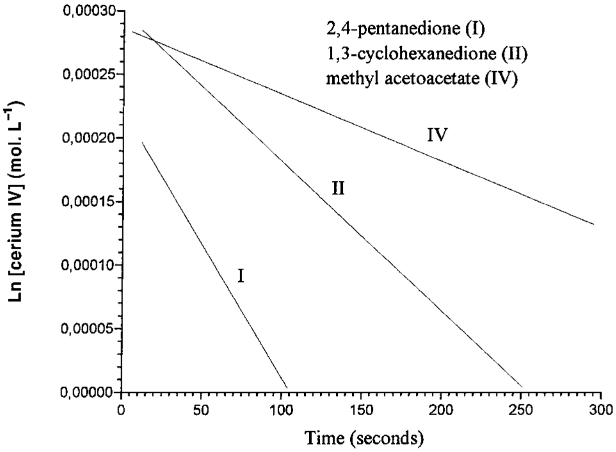

FIG. 3. Linear regression of the decay of Ce^{IV} UV-visible absorption for the substrates I, II, and IV.

Substrates V, VI, and VII showed negligible changes at the beginning and even after two hours.

We assume that the first step, the equilibrium formation of the substrate–Ce^{IV} complex, is rapidly reached and the second step, the oxidative first electron transfer from substrate to metal, is slower, and therefore it is the rate-determining step (first order kinetic) which can be followed by the fall of absorbance of the substrate–Ce^{IV} complex.

Thus, we recorded the decay at $\lambda_{max} = 302$ nm for I, II, and IV. For these substrates the range was wider than twice $t_{1/2}$. Ceric concentrations were determined by interpolation of λ_{max} absorption values from a Ce(IV) absorption vs concentration standard curve. This curve was constructed by modification of the titration of ceric sulfate described in literature (10). Several concentrations of ceric methanesulfonate, obtained by exhaustive electrolysis of the cerous salt, were titrated with a standard solution of potassium ferrocyanide using *N*-phenylanthranilic acid as indicator.

Linear plots of the natural logarithm of concentration vs time were obtained for I ($k_1 = 2.10 \cdot 10^{-6}\ s^{-1}$), II ($k_1 = 1.17 \cdot 10^{-6} s^{-1}$), and IV ($k_1 = 5.24 \cdot 10^{-7} s^{-1}$), with correlation coefficients (R) of 0.987, 0.992, and 0.983, respectively, as shown in Fig. 3.

The decay of Ce^{IV} absorption at $\lambda_{max} = 302$ nm for 1,3-diphenyl-1,3-propanedione III was almost the same as for 2,4-pentanedione I, although in an acetonitrile mixture solution. Thus, from Fig. 3, the following reactivity order can be established for these substrates: I $\approx$ III $>$ II $>$ IV $>$ V. The last one appears at the end of this order because it yields analogous products at a lower rate (6).

DISCUSSION

The β-diketones (I, II, and III), the β-ketoester (IV), and the β-diester (V) are electrooxidized by the mediator ceric methanesulfonate, uniformly producing good yields of fragmentation products with loss of CH_2. Methyl cyanoacetate (VI) and malononitrile (VII) proved to be unreactive. β-Dicarbonyls are essential to the success of the reaction.

Coulometry showed that 4 moles of electrons are consumed in these oxidations, and this stoichiometry is largely accepted in the literature as being responsible for a transformation of an active $-CH_2-$ group to a $C{=}O$ group in aqueous medium ($-4e$, $-4H^+$, $+H_2O$). A tricarbonyl intermediate is then obtained which, however, could not be detected in any of the present experiments. These derivatives may decompose chemically and not electrochemically in this reaction medium giving the obtained products and originating CO_2 (13) which could be identified in the electrolysis of I.

In a previous experiment, UV-visible spectroscopy showed that substrates I to IV exhibited enol absorption. When they were mixed with Ce^{III} salt VIII no product was formed. However, during the first seconds of reaction with Ce^{IV}, the color changed from yellow to dark red and important spectral modifications appeared (Fig. 2) in the charge transfer band corresponding to interaction between the ion and the ligand, indicating the formation of intermediate species. It is important to recall here that, in contrast to electrolysis where the mediator was present in small amounts, in kinetics studies the molar proportion was 1:1. No enol band appeared here during the first second in any reaction but the 200 to 280 nm regions were modified.

The $I \approx III > II > IV > V$ reactivity order shows that the substrates that are mainly in enol form, the β-diketones, are the most reactive. Ketoester, with less enol, is less reactive and the diester, which has no enol form, is least reactive.

We propose the initial formation of an enol–Ce^{IV} complex (and not an enolate–Ce^{IV} complex because the solution is very acidic) in a rapid equilibrium process that is not rate determining. The exponential decay of Ce^{IV} absorption observed in spectroscopic experiments indicates that the first electron transfer from enol to metal is a slow and rate determining and inner sphere process. Of course, spectroscopy could not show more than the transfer of one electron because the solution did not oxidize again as is the case for electrolysis.

Figure 1 shows that the absorptions in the 200 to 280 nm region are from Ce^{III} (f → d transition). After oxidation, there is a change in number and λ_{max} of the absorptions with a significant increase in intensity. As observed for several cerium salts and complexes, such as cerous nitrate and CAN, an increase of the number of ligands (11, 12) occurs in the oxidized state. Then, the modifications observed here can be attributed to the change in number and kind of some chemical bonds. By analogy with CAN ($(NH_4)_2Ce(NO_3)_6$), we may assume that the present compound in the oxidized solution is $Ce^{IV}(CH_3SO_3)_6^{2-}$. It is also postulated that CAN loses nitrate ligands when it is reduced ($Ce^{III}(NO_3)_5^{2-}$) (11). Consequently, it is possible that the structures of the complexes observed here are $Ce^{IV}(CH_3SO_3)_5(\text{substrate})^{-1}$ and, after electron transfer, $Ce^{III}(CH_3SO_3)_4(\text{substrate})^{-1}$. With these structures we propose that the ligand “substrate” is in the enol form, with the two oxygen atoms coordinately bound to the cerium complex; it would be reoxidized and continue the inner-sphere electron transfer .

Figure 4 shows a proposed mechanism for the formation of a substrate (exemplified here by I)–Ce^{IV} complex and the production of the tricarbonyl intermediate (2,3,4-pentanetrione).

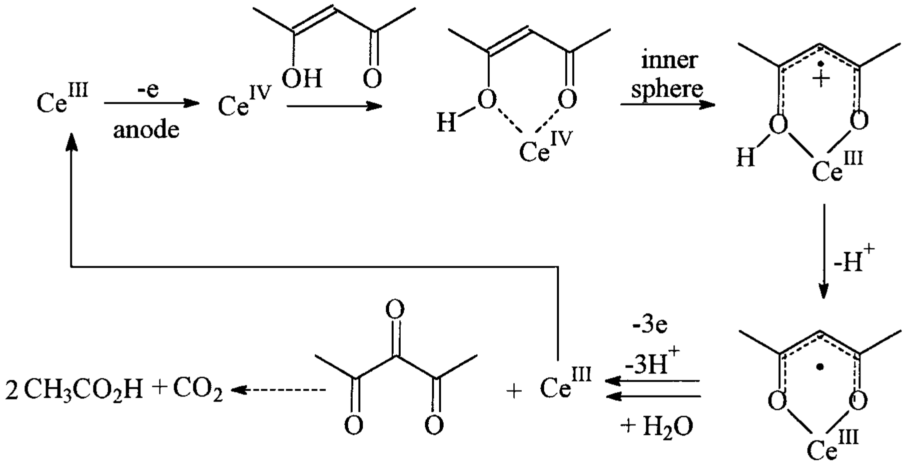

FIG. 4. Mechanistic proposition for the oxidation of β-dicarbonyl compounds with ceric methanesulfonate giving a tricarbonyl intermediate.

For the β-diketones I, II, and III, tricarbonylic intermediates decompose chemically yielding their respective carboxylic acids. Methyl acetoacetate produces acetic acid and, possibly, the unstable methyl dicarbonate, $HOCO_2CH_3$, which decomposes yielding CO_2 and methyl alcohol. The same intermediate could be produced by decomposition of the tricarbonyl product from the oxidation of V, exclusively producing methanol.

The difference between the reaction products obtained by oxidation of β-dicarbonyl substrates with CAN (or the ceric mediator from cerous nitrate) and those from $Ce^{IV}(CH_3SO_3)_5(\text{substrate})^{-1}$ is that in the first case they dissociate, yielding radicals in solution after the one-electron transfer from substrate to complex. These radicals react, producing dimers. In the present case the substrate–metal complex is maintained during the occurrence of the successive transfer of electrons ligand → metal, metal → anode, loss of protons and addition of H_2O, as suggested in Fig. 4. The complex formed by the oxidized β-dicarbonyl substrates $Ce^{III}(NO_3)_4(\text{substrate})^{-1}$ after the first electron transfer is unstable, whereas the $Ce^{III}(CH_3SO_3)_4(\text{substrate})^{-1}$ complex is more stable. This difference in stability can be explained on the basis of the hard and soft acid and base theory (14). The enol(soft base)–metal (hard acid) complexes can be dissociated easier by the substitution of nitrate bidentate ligands (15, 16), present in solution in large excess, because they are hard bases. The same complexes do not dissociate easily by substitution with methanesulfonate bidentate ligands, even when they are present in large excess in solution, because they are soft bases.

ACKNOWLEDGMENTS

We are grateful to FAPESP, CAPES, and CNPq for financial support.

REFERENCES

1. Molander, G. A., *Chem. Rev.* **92**, 29 (1992).
2. Baciocchi, E., and Ruzziconi, R., *in* "Free Radicals in Synthesis and Biology" (F. Minisci, Ed.), Series C: Mathematical and Physical Sciences, Vol. 260, p. 155. Kluwer Academic, Dordrecht, 1989.
3. Baciocchi, E., Ruzziconi, R., Giese, B., and Farshchi, H., *J. Org. Chem.* **55**, 5688 (1990).
4. Nair, V., and Mathew, J., *J. Chem. Soc. Perkin Trans.* **1**, 1881 (1995).
5. Cho, L. Y., and Romero, J. R., *Tetrahedron Lett.* **36**, 8757 (1995).
6. Cho, L. Y., and Romero, J. R., *Quim. Nova* **21**, 144 (1998).
7. Ye, S., and Beck, F., *Electrochim. Acta* **36**, 597 (1991).
8. Melikyan, G. G., *Synthesis* 833 (1993).
9. Zinner, L. B., *An. Assoc. Bras. Quim.* **30**, 27 (1991).
10. Vogel, A. I., *in* "Química Analítica Cuantitativa" (Kapelusz Ed.), Vol. 1, p. 423. Buenos Aires, 1960.
11. Torii, S., Tanaka, H., Inokuchi, T., Nakane, S., Akada, M., Saito, N., and Sirakawa, T., *J. Org. Chem.* **47**, 1647 (1982).
12. Martin, T. W., and Glass, R. W., *J. Am. Chem. Soc.* **92**, 5075 (1970).
13. Wolfrom, M. L., and Bobbit, J. M., *J. Am. Chem. Soc.* **78**, 2489 (1956).
14. Davies, J. A., and Hartley, F. R., *Chem. Rev.* **81**, 79 (1981).
15. Kochi, J. K., *in* "Free Radicals," Vol. 1, p. 632. Wiley-Interscience, New York, 1973.
16. Shwarz, H. A., *J. Phys. Chem.* **66**, 255 (1962).