ELECTROCATALYTIC OXIDATION OF β-DICARBONYL COMPOUNDS USING CERIC METHANESULPHONATE AS MEDIATOR

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β-dicarbonyl compounds were oxidized electrocatalytically, with fragmentation and loss of "CH_2", using ceric methanesulphonate as a mediator. 2,4-pentanedione yields acetic acid (90%), methyl acetoacetate yields acetic acid (84%) plus methanol and dimethyl malonate yields methanol (64%). For 1,3-diphenyl-1,3-propanedione and 1,3-cyclohexanedione, benzoic acid (61% yield) and glutaric acid (75% yield) were obtained, respectively. Methyl cyanoacetate and malononitrile were inert.

Keywords*: electrocatalysis; electrooxidation; ceric methanesulphonate.*

INTRODUCTION

In a recent letter[1] we reported the results of the chemical and electrocatalytic oxidation of some β-dicarbonyl and β-cyanocarbonyl compounds. Chemical oxidation were carried out using cerium ammonium nitrate, CAN ($(NH_4)_2Ce(NO_3)_6$) and the electrocatalytic ones using cerous nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, anodically oxidized to ceric) as a mediator. In the first set of experiments we obtained the saturated dimers, except for the cyano derivative which gave the unsaturated dimer, with yields varying from 61 to 80%. In the electrochemical set of experiments, only the unsaturated dimer with yields varying from 65 to 85% was obtained. The bond between the monomers was achieved by radical generation at the activated "CH_2" and the difference of reactivity, as postulated, was due to the steric hindrance of the dimer with respect to the size of CAN. Ceric ion generated electrochemically is less bulky and can promote the second oxidation yielding the unsaturated dimer.

We report here the electrocatalytic oxidation of some β-dicarbonyl compounds by cerous methanesulphonate $Ce(CH_3SO_2)_3$[2], anodically oxidized to ceric ion, and some considerations that allow to compare these results with those previously reported. The chosen substrates were the β-diketones, 2,4-pentanedione, 1,3-cyclohexanedione, 1,3-diphenyl-1,3-propanedione; the esthers, methyl acetoacetate, dimethyl malonate and methyl cyanoacetate and malononitrile, a β-dinitrile. This way, we have studied several combinations of β-dicarbonyl compounds and related functions.

EXPERIMENTAL

Preparation of cerous methanesulphonate

3.84g (39.6 mmol) of methanesulphonic acid was added dropwise to a 14.0mL of water suspension of 3.0g (8.8 mmol) of cerous carbonate. When the evolution of CO_2 stopped, the mixture was filtered using diatomite layer. Solution was evaporated at 90°C and the white solid, cerous methanesulphonate, was washed with acetone and dried at vacuum pump to constant weight (4.1g, 68% yield)[3].

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Preparation of ceric methanesulphonate

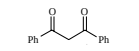
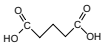
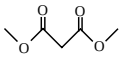
Electrolyses was carried out in a cylindric cell with 50mL of capacity using a platinum gauze with an area of 164cm^2 (diameter 0.16mm) as the working electrode and a platinum wire with 1 cm^2 area, within a syntherized glass tube, as the auxiliary electrode. The reference electrode was a saturated calomel electrode (SCE). A Potentiostat / Galvanostat PAR model 273 or FAC model 200A was used and current was recorded in an Intralab Recorder model 2030. A potential of +1.5V vs. SCE was applied to 30mL of a solution of 0.5 $mol.L^{-1}$ in methanesulphonic acid and 0.05 $mol.L^{-1}$ in cerous methanesulphonate to transform all Ce(III) into Ce(IV) (145 Coulombs).

Mediated oxidation of the substrates

672mg of 1,3-diphenyl-1,3-propanedione (3mmoles), or 224mg of 1,3-cyclohexanedione (2mmoles), or 200mg of 2,4-pentanedione (2mmoles), or 232mg of methyl acetoacetate (2mmoles), or 396mg of dimethyl malonate (3mmoles), or 198mg of methyl cyanoacetate (2mmoles) or 198mg of malononitrile (3mmoles) were added to the solution of ceric methanesulphonate in the cell described above, and the same potential of +1.5V vs. ECS was applied. It was necessary to use a mixture of 4:1 of acetonitrile and a methanesulphonic acid solution to dissolve 1,3-diphenyl-1,3-propanedione. Electrolyses were carried out until the current fell to residual values (less than 1mA) in all cases, corresponding to four Faradays of charge consumption. Crude product was extracted with 50mL of ethyl ether by a liquid-liquid extractor for 24 hours. For 1,3-diphenyl-1,3-propanedione and 1,3-cyclohexanedione, the solvent was dried and evaporated and the white crystals obtained were washed with ethyl ether, dried, analyzed and identified by melting point, ^{1}H-RMN, ^{13}C-RMN and FTIR.

For the other products, the ethereal solution was analyzed chromatographically. The peaks were identified qualitatively by comparison with an original sample of acetic acid and methanol. Quantitative analysis was made by comparing the areas of the peaks of a known volume injected with the areas and volume of standard solutions of those substances. Gas-chromatography were performed in an Intralab Chromatograph and Integrator model 3300 with an OV17 column. Initial temperature 35°C, 5 minutes as isotermic condition and temperature program with a ratio of 10°C /minute and 200°C as final temperature. Injector and detector temperature: 250°C and 300°C.

Table 1. Substrates oxidation at +1.5V vs. SCE constant potential.

Substrates	Reaction time and charge needed consumed	Initial current	Products and yield
 1,3-diphenyl-1,3-propanedione 3mmoles	48 hours 1187C (102% for 4F/mol)	58mA	 61% (a)
 1,3-cyclohexanedione 2mmoles	47 hours 750C (97% for 4F/mol)	83mA	 75% (a)
 2,4-pentanedione 2mmoles	40 hours 778C (100% for 4F/mol)	90mA	 90% (b)
 methyl acetoacetate 2mmoles	42 hours 744C (96% for 4F/mol)	70mA	 84% (b) and methanol (c)
 dimethyl malonate 3mmoles	57 hours 1056C (91% for 4F/mol)	69mA	H_3C-OH 64% (b)

(a) yield for purified products; (b) chromatographic yields; (c) variable yield for each experiment.

RESULTS AND DISCUSSION

Methyl cyanoacetate and malononitrile were inert. The residual current is from the solution. The other substrates were oxidized and the results are shown in table 1.

Benzoic acid (61% yield, mp: 121-123ºC (lit.122.4ºC[4a]) was obtained from 1,3-diphenyl-1,3-propanedione. Glutaric acid (75% yield), mp: 94-97ºC (lit.99ºC[4b]), ^{1}H-RMN (80MHz, CCl_3D), δ 1.6-2.7(6H, m), 10.2(2H, s), ^{13}C-RMN (APT, 20MHz, CCl_3D) δ 21.2(CH_2), 33.8(CH_2), 176.4(C=O), FT-IR (KBr) ν 3436(S, broad), 1717(S) was obtained from 1,3-cyclohexanedione.

2,4-Pentanedione yields acetic acid (90%), methyl acetoacetate yields acetic acid (84%) plus methanol (it was not possible to quantify it) and dimethyl malonate yields methanol (64%).

No other products were found for these oxidations. There was molecular degradation in all cases with loss of "CH_2". As charge equivalent for 4F.mol^{-1}, typical for a transformation of a "CH_2" to a carbonyl group[4], was consumed, one can assume that a tricarbonyl intermediate was formed which was decomposed in the reactional medium yielding the related products. The presence of two carbonyls seems to be fundamental because substrates containing nitrile groups were unreactive. We observed extensive change in the color of the solution from yellow (characteristic for Ce(IV) ion) to dark red when β-diketones were added and it disappeared after some minutes yielding a colorless solution. The other carbonylic substrates did not present this behavior.

It is interesting to observe the change of behavior from chemical oxidation with CAN and electrochemical oxidation with the ceric nitrate/nitric acid system to ceric methanesulphonate/methanesulphonic acid system. The first allowed radical coupling yielding dimeric product and with the reported system, "CH_2" oxidation and further degradation were obtained.

CONCLUSION

These results show that ceric oxidants, used as mediators in electrocatalytic oxidation of β-dicarbonyl compounds, give different products, depending on their ligands and solvents. These results can be useful in the case of the β-keto substrates, for analytical degradation and simplification of complex structures and for synthetic purposes.

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