



Electrosynthesis, spectral and structural studies of a semi-conducting oligomer deriving from a methoxy-substituted chalcone



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ABSTRACT

The anodic oxidation of a substituted chalcone namely the (E)-1-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-enone (TMC) was investigated by different electrochemical techniques using a platinum working electrode in acetonitrile. On the cyclic voltammetry time scale, the TMC exhibited a single irreversible anodic peak around 1.4 V vs. Ag/AgCl and the coupling of the radical cations, issued from the first electron transfer, was the governing reaction near the electrode. Electrolysis at a constant potential revealed that an oligo o-phenylenevinylene was the main product of the anodic oxidation of TMC. The chemical structure of the isolated oligomer was elucidated by ¹H, ¹³C NMR, and IR spectroscopy. Gel permeation chromatography indicated that the average chain length was about 5 units. In addition, the obtained oligomer was thermally stable up to 220 °C and exhibited a light emission in the indigo-blue region. Finally, a mechanism for the TMC electro-oligomerization was proposed on the basis of the electrochemical data and the theoretical calculation of the spin densities distribution for the TMC radical cation.

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1. Introduction

Chalcone derivatives are important and interesting natural compounds that can be easily prepared in the laboratory. Usually, they are synthesized by the aldol condensation between substituted benzaldehydes and acetophenones in hydro-alcoholic medium in the presence of sodium hydroxide as a catalyst [1]. Chalcones are widely used for their anti-tumor, anti-carcinogenic, anti-bacterial, anti-ulcer and anti-inflammatory activities [1–5]. Moreover, they have been recently used in the field of material science for non-linear optics, electrochemical and optical chemosensing [6–13].

The chemical oxidation of chalcones was well studied. In this frame, various reagents and catalytic systems were described in the literature. Among them are: Lead Tetraacetate and Manganic Acetate [14], Ru (III)/V (V) [15], Ceric ammonium nitrate (CAN)/O₂ [16], iron–salen complex/hydrogen peroxide [17] and OsO₄–Ce⁴⁺ [18].

In all these cases either the >C=C< or >C=O group of the chalcone was attacked leading to different oxidative cleavage products. Mainly, the initial benzaldehyde and ketone as well as their corresponding oxidation products (Benzoic acid, Phenyl acetaldehyde and epoxides) were the resulting products. On the other hand, few researches were devoted to the anodic oxidation of chalcones [19–21]. Particularly, flavones and flavanonols were described as the resulting compounds of the anodic oxidations of 2'-hydroxychalcones [19,20].

In this work, we are interested on the investigation of the anodic oxidation of a methoxylated chalcone namely the (E)-1-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)prop-2-enone (TMC). In previous work [22–29], we showed that the presence of the methoxy group(s) has an important effect on lowering the oxidation potential and on directing the reactional scheme. Particularly, it promoted the coupling reactions leading to oligomers formation [24–29]. This study was carried out in acetonitrile and on a platinum electrode at an analytical and synthetic scale using cyclic voltammetry and controlled potential electrolysis, respectively. The main electrolysis product was characterized by different physicochemical method (NMR ¹H, NMR ¹³C, IR, UV-visible and ATD-

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ATG). Finally, a mechanism for the anodic oxidation of TMC was evoked in the light of a theoretical DFT calculation.

2. Experimental section

2.1. Materials and instrumentation

The p-methoxyacetophenone and the ferrocenecarboxaldehyde, used in this work, were obtained from «ACROS ORGANICS». The 3,4,5-trimethoxybenzaldehyde and benzaldehyde were procured from «ALDRICH». Acetonitrile CH₃CN (PANREAC) was distilled on calcium hydride CaH₂ under Argon. Tetrabutyl ammonium tetrafluoroborate (TBAF), used in the voltammetric study, was prepared and purified in the same way as in Ref. [22]. The tetraethyl ammonium tetrafluoroborate (TEAF), used in the preparative electrolysis, was provided by ALDRICH.

The voltammetric study was performed with a Voltalab10 apparatus from Radiometer driven by the Volta Master software. All cyclic voltammetric measurements were conducted at room temperature (25 ± 1 °C) in 25 mL of CH₃CN solution containing TBAF (0.1 M) as a supporting electrolyte. A three-electrode cell was used for electrochemical oxidation under an inert atmosphere by saturation with high purity nitrogen gas. The working electrode was a 2 mm diameter platinum disk (Tacussel type EDI). The reference electrode was an Ag/AgCl/3 M KCl electrode. The counter electrode was a Pt wire. The measurements were carried out with six different potential scan rates (20–500 mVs⁻¹) and four concentration (5 × 10⁻⁴–5 × 10⁻³ M). The ohmic drop compensation was activated during the experiments.

The number of exchanged electrons (*n_e*) at the first oxidation peak of substrat (TMC) was obtained from the comparison of the peak current to the mono-electronic oxidation peak of the prepared ferrocenylchalcone recorded in the same previously described conditions.

The preparative electrolyses were carried out with 10⁻¹ M TMC solution in a two-compartment cell, under nitrogen, at a controlled potential. A potentiostat (Tacussel PRT 100-1X) was used together with an integrator (Tacussel IG5). The electrolysis cell was separated with a number 4 glass frit. The working electrode was a 4 cm² platinum grid. A Pt wire, placed in a separate compartment, constituted the counter electrode. The working electrode potential was adjusted versus an Ag/AgCl/3 M KCl reference electrode. The electrolysis solutions were evaporated under vacuum until elimination of the major part of acetonitrile, and the electrolysis products were extracted with chloroform. The organic solution, was dried with anhydrous Magnesium Sulfate (MgSO₄), concentrated and then precipitated in diethyl ether under stirring. The isolated compound was identified by different physico-chemicals methods.

The ¹³C and ¹H NMR studies were carried out with a Bruker 300 MHz in deuterated chloroform CDCl₃. The IR analysis was performed with a Shimadzu 8400–Fourier Transform spectrophotometer. The spectra were obtained with KBr pressed pellets (4000–500 cm⁻¹). UV-vis spectrophotometric measurements were performed with a Shimadzu spectrophotometer. The photoluminescence spectrum was collected from the front-face geometry of the samples with a Jobin-Yvon Fluorolog spectrometer using Xenon lamp (500 W) as an excitation source (λ_{ex} = 330 nm).

For the gel permeation chromatography analysis, a μ styragel 500 A–15 μm column was used (with a length of 300 mm and a diameter of 7.8 mm). The temperature was 30 °C. The solvent was tetrahydrofuran with a flow rate of 0.85 mL min⁻¹. Polystyrene was used as a standard.

The thermogravimetric analysis was carried out in a Perkin-Elmer TGS-1 thermal balance with a Perkin-Elmer UV-1 temperature program control. The samples were placed in a platinum

sample holder and the thermal degradation measurements were carried out between 0 and 500 °C at a speed rate of 10 °C min⁻¹ under nitrogen.

2.2. General procedure

2.2.1. Synthesis of (E)-1-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl) prop-2-enone (1)

TMC (1, Scheme 1) was synthesized following the previous reported procedure [30]. Spectroscopic properties were in agreement with those described earlier [31]. The TMC crystal structure was reported in Ref. [32].

2.2.2. Synthesis of (E)-1-(4-methoxyphenyl)-3-(ferrocenyl) prop-2-enone (2)

The ferrocenylchalcone (FC) (2, Scheme 1), chosen as a reference in cyclic voltammetry, was prepared directly from ferrocenecarboxaldehyde and acetophenone according to the previously described procedure [33]. A red colored powder was obtained in 62% yield, m. p = 124 °C. ¹H NMR (300 MHz, CDCl₃) δ_H (ppm): 4.19 (s, 5H), 4.49 (s, 2H), 4.60 (s, 2H), 7.13 (d, 1H, *J* = 15.3 Hz), 7.47–7.59 (m, 3H), 7.75 (d, 1H, *J* = 15.3 Hz), 7.98 (d, 2H, *J* = 7.2 Hz). ¹³C NMR (75 MHz, CDCl₃) δ_C (ppm): 69.06, 69.84, 71.41, 119.24, 128.38, 128.56, 132.39, 146.86, 188.60. The electrochemical properties of the FC were measured at a platinum working electrode in acetonitrile 10⁻¹ M TBAF solution. The cyclic voltammetry analyses showed a reversible one-electron oxidation (*E_{pa}* = 0.596 V vs. Ag/AgCl at *v* = 0.1 V s⁻¹) with a peak potential separation (Δ*E_p*) near to 0.06 V and an anodic to cathodic current ratio close to unity, irrespective of changing sweep rate.

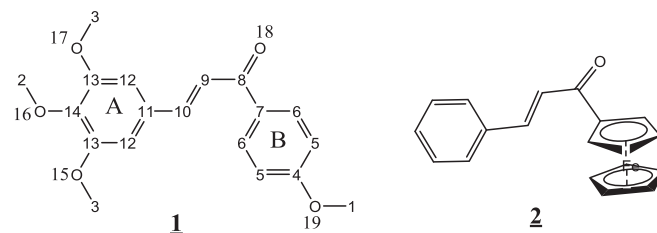
2.3. Method of calculations

All calculations for the oxidized TMC have been performed using the most popular Becke's three-parameter hybrid functional, B3 [34], with non-local correlation of Lee–Yang–Parr, LYP, abbreviated as B3LYP, method [35]. This method, based on Density Functional Theory (DFT) for a uniform electron gas (local spin density approximation), is used with the 6-31g(d,p) basis set. An open-shell spin-unrestricted formalism was used for oxidized structure with unpaired electrons (UB3LYP). All calculations reported in this work were carried out with Gaussian 98 program [36].

3. Results and discussion

3.1. Voltammetric study

The voltammetric study of TMC was carried out in CH₃CN (0.1 M TBAF) on a platinum disk for different product concentrations and at different scan rates ranging from 20 to 500 mVs⁻¹. At a scanning rate of 100 mV s⁻¹ and for a substrate concentration *C* = 10⁻³ M, the recorded cyclic voltammogram exhibited a single irreversible anodic peak at 1.347 V vs. Ag/AgCl, as shown in Fig. 1.



Scheme 1.

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