

The anodic reactivity of 4,4'-dimethoxychalcone: a synthetic and mechanistic investigation

Imen Aribi¹ · Sahbi Ayachi² · Kamel Alimi² · Sadok Roudesli¹ · Ayoub Haj Said¹

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Abstract The anodic oxidation of the 4,4'-dimethoxychalcone (DMC) was investigated by different electrochemical methods at a platinum working electrode and in acetonitrile as a solvent. The DMC exhibited a single irreversible anodic peak around 1.6 V versus Ag/AgCl. On the time scale of cyclic voltammetry experiments, the highly reactive radical cation issued from the first electron transfer underwent a second order rate-limiting reaction. The potential imposed electrolyses of DMC led to the formation of a semi-conducting oligomer with 40 % yield. Using different physico-chemicals methods, the structural study confirmed the formation of an o-phenylenevinylene oligomer. The values of the corresponding optical and electrochemical band gaps were calculated to be 3.15 and 2.86 eV, respectively. Finally, a mechanism for the DMC electro-oligomerization was proposed on the basis of the obtained results.

Keywords Anodic oxidation \cdot Chalcone \cdot Radical cation \cdot Conjugated oligomers \cdot Photoluminescence

Introduction

In previous studies, we were interested in the anodic oxidation of substituted methoxy-substituted arenes at a platinum electrode in acetonitrile [1, 2]. We demonstrated that the coupling of the radical cations issued from the first electron transfer was the governing reaction near the electrode. Particularly, under anhydrous

Ayoub Haj Said ayoub.hajsaid@fsm.rnu.tn

¹ Laboratoire Interfaces et Matériaux Avancés, Faculté des Sciences de Monastir, Université de Monastir, 5000 Monastir, Tunisia

² Unité de Recherche (UR 11ES55), Matériaux Nouveaux et Dispositifs Electroniques Organiques, Faculté des Sciences de Monastir, Université de Monastir, 5000 Monastir, Tunisia

conditions, successive coupling reactions, according to an (EC)n mechanism, led to conjugated oligomers from the polyphenylene family [3–8]. The methoxy group plays a crucial role in decreasing the oxidation potential and in the distonic character displayed by the generated radical cations. In the present work, we are interested in the anodic oxidation of a substituted chalcone, containing the methoxyphenyl moiety. In fact, chalcones belong to a class of α , β -unsaturated ketones possessing highly conjugated alkenyl and carbonyl groups between two phenyl rings. They are important and interesting natural compounds that can be easily prepared in the laboratory. Recently, chalcone derivatives have been used in the field of material science for non-linear optics, electrochemical and optical chemosensing [9–16].

Although their electrochemical reduction has been well studied [17-20], few researches have been devoted to the anodic oxidation of chalcones [21-24]. Flavones and flavanonols have been described as the resulting compounds of the anodic oxidations of 2'-hydroxychalcones [21-23]. On the other hand, the oxidation of chalcones by different chemical agents leads to their cleavage [25-28] and to the olefinic double bond hydroxylation [29].

In this work, 4,4'-dimethoxychalcone (DMC) was studied. The investigation of the electrochemical behavior of this product was carried out on an analytical and a synthetic scale with cyclic voltammetry and potential imposed electrolysis, respectively. The chemical structure of the electrolysis products was characterized by different physico-chemical methods.

Materials and methods

Chemicals

Acetonitrile CH₃CN (PANREAC) was distilled on calcium hydride CaH₂ under Argon. Chloroform was obtained from PROLABO and diethyl ether from PANREAC. Tetrabutylammonium tetrafluoroborate (TBAF) used in the voltammetric study was prepared and purified in the same way as in Ref [1]. The tetraethyl ammonium tetrafluoroborate (TEAF) used in the preparative electrolysis was procured from ALDRICH.

The p-methoxyacetophenone, the p-anisaldehyde and the ferrocenecarboxaldehyde used in this work were provided by 'ACROS ORGANICS'. All other used reagents were commercially available and were used as received.

Synthesis of chalcones

The substituted chalcone DMC 1 (see Scheme 1) was prepared according to a standard procedure of the base-catalyzed Claisen–Schmidt condensation by the addition of a small amount of aqueous sodium hydroxide to an ethanolic equimolar solution of a p-anisaldehyde and a p-methoxyacetophenone. Stirring was continued for 2 h, after which the chalcone crystallized. The mixture was chilled in ice for 10-15 min, filtered on a Buchner funnel, and the precipitate was successively



Scheme 1 The chemical structures of 4,4'-dimethoxychalcone (DMC) 1 and ferrocenylchalcone (Fc-chal) $\mathbf{2}$

washed with water until the washings were neutral, and then it was washed with icecold ethanol. After drying, the product was recrystallized from 95 % ethanol to afford the chalcone. A yellowish powder was obtained in 80 % yield. The completion of the reaction was monitored by thin layer chromatography.

¹H NMR (δ/ppm): 8.02 (d, 2H, J = 8.7 Hz)–7.77 (d, 1H, J = 15.6 Hz)–7.69 (d, 2H, J = 8.7 Hz)–7.42 (d, 1H, J = 15.6 Hz)–6.97 (d, 2H, J = 9 Hz)–6.93 (d, 2H, J = 8.7 Hz)–3.88 (s, 3H)–3.85 (s, 3H). ¹³C NMR (δ/ppm): 55.46–55.54–113. 83–114.83–119.59–127.85–130.15–130.75–131.40–143.86–161.55–163.31–188.82. M.p = 88 °C.

The ferrocenylchalcone Fc-chal 2 (see Scheme 1), chosen as a reference in cyclic voltammetry, was prepared directly from ferrocenecarboxaldehyde and acetophenone according to the previously described procedure [30]. A red powder was obtained in 62 % yield.

¹H NMR (δ/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 (δ/ppm): 69.06–69.84–71.41–119.24–128.38–128.56–132.39–146.86–188.60. M.p = 124 °C.

The electrochemical properties of the Fc-chal were measured at a platinum working electrode in acetonitrile 10^{-1} M TBAF solution. The cyclic voltammetry analyses showed a reversible one-electron oxidation at $E_{\rm pa} = 0.596$ V versus Ag/AgCl when v = 0.1 Vs⁻¹ (Fig. 1). The peak potential separation ($\Delta E_{\rm p}$) was close to 0.06 V and the anodic to cathodic current ratio was equal to unity, irrespective of changing sweep rate.

Electrochemistry

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 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 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 in the region of 20–500 m Vs⁻¹. The ohmic drop compensation was activated during the experiments.



Fig. 1 Cyclic voltammogram for oxidation of Fc-chal, 10^{-3} M in CH₃CN, 10^{-1} M TBAF, recorded at a platinum disk electrode (2 mm diameter). Potential scan rate: 100 m Vs⁻¹, Counter electrode: Pt wire

The preparative electrolyses were carried out with 10^{-1} M 4,4'-dimethoxychalcone solution in a two-compartment cell, under nitrogen, at a controlled potential. The potentiostat (PRT 100-1X) and the current integrator (IG5-LN) were both procured from Tacussel. 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 $MgSO_4$, concentrated and then precipitated in diethyl ether.

Material characterization

An infrared (IR) analysis was performed with a Shimadzu 8400–Fourier Transform spectrophotometer. The spectra were obtained with KBr pressed pellets $(4000-500 \text{ cm}^{-1})$.

¹³C and ¹H nuclear magnetic resonance (NMR) studies of the monomer and oligomer were carried out with a Bruker 300 MHz in deuterated chloroform CDCl₃.

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 ($\lambda = 330$ nm).

A μ styragel 500 A–15 μ m column was used in gel permeation chromatography (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.

Results

Voltammetric study

The voltammetric study of DMC 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 m Vs⁻¹. A reproducible voltammetric pattern was obtained with a single irreversible anodic peak. At 100 m Vs⁻¹ and for a substrate concentration $C = 10^{-3}$ M, the corresponding oxidation peak potential was 1.586 V versus Ag/AgCl, as shown in Fig. 2.

In order to obtain a better understanding of the electrochemical process, the variation of the peak potential of DMC with the scan rate or substrate concentration was studied. The peak potential variation is a linear function of both the logarithms of the potential scan rate v and the DMC concentration (C_i). The slopes are close to 20 mV and -20 mV per decade of v and (Ci/v), respectively (Figs. 3, 4). These results indicate that the first electron transfer is fast, and is followed by a rate-determining second-order homogeneous reaction.

On the other hand, an approximate determination of the number of exchanged electrons (n_e) was achieved using the equations given in the literature [31]. This was obtained from the comparison of the peak current of DMC to the one of the



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Fig. 3 Variation of the peak potential as a function of the logarithm of the scan rate for DMC in CH₃CN, 10^{-1} M TBAF, recorded at a platinum disk electrode **a** C = 5 × 10⁻⁴ M; **b** C = 10⁻³ M; **c** C = 2 × 10⁻³ M; **d** C = 5 × 10⁻³ M



Fig. 4 Variation of the peak potential as a function of the log (C/v) (*C* concentration in M, *v* potential scan rate in Vs⁻¹) for DMC in CH₃CN, 10^{-1} M TBAF, recorded at a platinum disk electrode

monoelectronic ferrocene/ferrocenium redox system of the Fc-chal recorded in the same conditions (Figs. 1, 2). In fact, the peak currents for DMC and Fc-chal are described by Eq. (1) and (2), respectively.

$$Ip_{DMC} = 0,527 n_e^{3/2} F A (F/RT)^{1/2} D_{DMC}^{1/2} C_{DMC} v^{1/2}$$
(1)

$$Ip_{Fc-chal} = 0,446 n_1^{3/2} F A (F/RT)^{1/2} D_{Fc-chal}^{1/2} C_{Fc-chal} v^{1/2}$$
(2)

With, Ip, C and v correspond to peak current, substrate concentration and potential scan rate, respectively. n_e and n_1 are the number of the exchanged

electrons for DMC and Fc-chal, respectively. Actually, $n_1 = 1$ for the monoelectronic Fc-chal electrochemical system. Taking no account of the difference between the diffusion coefficients D_{DMC} and $D_{\text{Fc-chal}}$, n_{e} was then deduced by combining Eqs. 1 and 2:

 $n_{\rm e}^{3/2} = 0,446/0,527 \left[{\rm Ip_{DMC}}/{\rm Ip_{Fc-chal}} \right] \left[{\rm C_{Fc-chal}}/{\rm C_{DMC}} \right] \left[v/v \right]^{1/2}$

 $n_{\rm e}$ value was calculated to be close to one electron.

Preparative scale electrolysis

In the light of the cyclic voltammetry results, DMC preparative electrolyses were performed at a fixed potential located at 1.600 V versus Ag/AgCl reference electrode in a divided cell. Homogenization of the electrolytic solution was assured by a magnetic stirring under nitrogen. The oxidative electrolyses were stopped after consumption of 2F/mole of the starting material. The brown dark solution obtained at the end of the electrolysis was treated as described in the experimental section. After precipitation in diethyl ether, a brown powder P1 was collected by filtration and dried under vacuum. The rough yield calculated from the ratio of the collected powder weight by that of the DMC starting material was around 40 %. P1 is soluble in common organic solvents such as chloroform, dichloromethane and acetone.

Structure characterization of the electrolysis product P1

The collected powder P1 was characterized by different physico-chemical techniques. Firstly, the ¹H NMR spectrum of DMC (Fig. 5a) in deuterated chloroform was recorded. This spectrum showed multiplet resonance signals at chemical shift 6.90–8.05 ppm corresponding to the aromatic protons. Doublets of the ethylenic protons appeared at 7.77 ppm (J = 15.6 Hz) and 7.42 ppm (J = 15.6 Hz). The peaks at 3.85 and 3.88 ppm were assigned to the methoxy protons.

The electrosynthesized powder spectrum (Fig. 5b) exhibited two broad resonance peaks, at the same shift as the DMC's spectrum, attributed to the methoxy and aromatic protons. These large signals are characteristic of polymeric material. The GPC analysis confirmed that P1 was a short-chain oligomer with Mw = 1040 and Mn = 919 corresponding to an average degree of polymerization (DP) close to 4 and a dispersity of 1.1.

The ¹³C NMR spectra of DMC and the oligomer P1 are given in Figs. 6 and 7, respectively. Carbons of DMC were assigned as depicted by Fig. 6. Both spectra presented a great similarity. However, we note that the ethylenic carbons peaks (C_6 at 119.59 ppm and C_7 at 143.86 ppm) were sharply attenuated in the oligomer spectrum.

Moreover, the broad signal in the aromatic region around 130–135 ppm, in the oligomer spectrum, revealed that aromatic carbons were involved in the oligomerization reaction. The ¹³C NMR spectrum recorded with DEPT using a 135° pulse

angle (Fig. 7b) showed that signals corresponding to quaternary carbons were merged with this broad signal at 130–135 ppm. Finally, we note the presence of new weak and well-resolved signals appearing around 23, 42 and 170 ppm.

The IR spectra of DMC and the oligomer are given in Fig. 8. The position of various vibration bands and their attribution are given in Table 1. It is worth noting that the bands located at 990 and 525 cm^{-1} , observed with DMC, completely



Fig. 5 ¹H NMR spectra of the DMC (a) and the collected powder (b) (*asterisk* denote the signals of diethyl ether and $CDCl_3$)





200 180 160 140 120 100 80 60 40 20 ppm Chemical shift [ppm]

Fig. 7 ¹³C NMR spectrum of the oligomer P1



Fig. 8 FT-IR spectra of DMC (a) and the oligomer P1 (b)

Table 1 Positions and assignments of different bond vibrations of DMC and	P1
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Mode assignment	Wavenumber [cm ⁻¹]	
	DMC	P1
C–H stretching	3052	3024
CH ₃ –O– protons stretching	2969-2857	2960-2859
C=O stretching	1660	1680
C=C stretching	1602-1513	1607–1516
-C-H (CH ₃) deformation	1418	1458
C–O–C stretching	1020-1260	1030-1260
C=C-H ethylenic out of plane deformation	990	Absent
C=C-H aromatic out of plane deformation	820	839
C=C ethylenic out of plane deformation	525	Very weak

vanished in the oligomer spectrum. These bands are characteristic of the out of plane deformation of H–C bond (HC=CH, E configuration) and the C=C bond of the ethylenic group, respectively [32].

Optical study

The UV-visible absorption spectra of the DMC and the oligomer P1 in chloroform are given in Fig. 9. The DMC spectrum showed two absorption maxima at 335 nm (B I, π - π * transition) and 232 nm (B II, n- π *). The B I was attributed to the substituted cinnamoyl chromophore (ArCH=CH-CO-) involving the whole conjugated system corresponding to the intramolecular charge transfer from the electron-



Fig. 9 UV-visible absorption spectra of DMC (a) and the oligomer P1 (b) in chloroform solution

donor methoxy substituent to the carbonyl group acting as an electron acceptor. B II was assigned to the substituted benzoyl chromophore (ArCO–). The oligomer spectrum exhibited two absorption bands with maxima located at 222 and 279 nm. Moreover, the spectrum presents a shoulder at 335 nm.

A preliminary photoluminescence study revealed that when an oligomer powder was excited with a 330 nm wavelength laser radiation, it showed a light emission with λ_{max} located around 390 nm (Fig. 10). The broad emission spectrum could be related to the presence of oligomers with different conjugation lengths [33].

Thermal analysis

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were used to study the oligomer thermal degradation. The obtained results are shown in Fig. 11. TGA measurements revealed that synthesized material had a satisfactory thermal stability until 500 K. It should be noted that a small weight loss (around 5 %) from ~ 300 to ~ 500 K was observed, most probably related to evaporation of the residual solvents used during oligomer purification. Beyond this zone of thermal stability, two fast degradations were found: the first occurred from ~ 500 to 648 K with a maximum weight loss of nearly 28 %, and the second fastest degradation starting from 648 K.

Discussion

The obtained results supported the formation of a semiconducting conjugated material as the main product of the chalcone oxidation. Indeed, the voltammetric study indicated that the rate-limiting step is the coupling of two radical cations issued from the first electron transfer. This assumption is in agreement with an



Fig. 10 Photoluminescence spectrum of P1



Fig. 11 TGA and TDA thermograms of electro-synthesized oligomer P1

electronic stoichiometry close to one electron at the time scale of the voltammetric experiments. It is accepted that the electropolymerization of aromatic and heteroaromatic rings occurs by a general (EC)n mechanism, where E and C represent the electron transfer and chemical reaction steps, respectively. The NMR and the Fourier transform infrared spectroscopy (FTIR) studies corroborated that the phenyl ring (A) and the chalcone double bond were both involved in the coupling reaction. Actually, the vanishing of the corresponding CH signals in the ¹³C NMR spectra

and the characteristic bands in the infrared spectra confirmed this deduction. This phenyl-vinyl cross-linking reaction of DMC molecules led to a phenylene vinylene like oligomer. This non-symmetric linkage was induced by the distonic effect displayed by the methoxy group as described in earlier works [1, 2]. In fact, the structure of the radical cation of DMC can be described by two mesomeric forms involving the donating effect of the methoxy group (I and II in Scheme 2). This intuitive assumption has been corroborated by a recent theoretical calculation of the charge and the spin density distributions for the DMC radical cation [34]. This latter study, showed that the highest spin densities were located on carbons $C_{5'}$ and C_{6} . The non-symmetric coupling of two radical cations appears to give a better compromise between steric and electronic effects. Consequently, the $C_{5'}$ - C_6 crosslinking led, after a proton loss, to the intermediate III as described by the mechanism given in Scheme 2. This intermediate rearranges to give the dimers V. This rearrangement, previously described for a similar case [1], is accomplished with aromatization as driving force and occurs in a similar way to the acid catalysed rearrangement of 4.4' disubstituted cyclohexadienones [35, 36]. However, it is very difficult to describe rigorously the dimers structure because of the complexity of the possible stereostructures related to the trans-cis configuration. This structural issue is further complicated by the presence of possible rotamers (s-cis/s-trans) relative to the conformation of the carbonyl groups.

The subsequent oxidation of the resulting dimers V, at the electrolysis time scale, results in further coupling (chain growth) with other oxidized monomers, dimers, or oligomers. The observed low degree of polymerization could be partially explained by the presence of a side reaction limiting the chain growth. In Scheme 3, we depicted a plausible mechanism for the corresponding process. Accordingly, the oxidized C=C bond is subjected to the solvent attack to form an acetamide. This Ritter-like reaction is well known when electrolyses are carried out in acetonitrile, particularly for ketone anodic oxidation [37]. Simultaneously, a stabilized free radical was formed on the oligomer. The latter, could undergo a hydrogen atom abstraction from the solvent [37] to afford a keto-enol system. The new signals appearing around 23, 42 and 170 ppm, in the oligomer ¹³C spectrum, supported the introduction of the acetamide moiety in the oligomer structure. These signals could be attributed to the aliphatic and to the carbonyl carbons of the acetamide.

Despite this limited chain growth, the semi-conducting character of the obtained material was confirmed by the optical study. In fact, in the UV-visible absorption spectrum, the band located at 335 nm is attributed to the ArC=C-CO-Ar conjugated system absorption in a similar way to the starting chalcone. However, the band located at 279 nm is assigned to the conjugated backbone. This low value resulted most probably from the less extended conjugation due to the short chain length, the lack of planarity and to the stereostructure irregularity. A very similar UV spectrum was observed for oligo o-phenylene vinylene [38]. The optical band gap of the oligomer was calculated from the onset of absorption and the energy band gap was estimated to be 3.15 eV for the oligomer in solution. In addition, the electrochemical study of oligomer was used to calculate the HOMO, LUMO and the electrochemical band gap [39, 40]. The corresponding values were estimated to be -5.82, -2.96 and 2.86 eV, respectively.



Scheme 2 The mechanism of dimer formation

In addition, the emission spectrum of the oligomer exhibited a large band with a maximum at 390 nm. The band broadness revealed the presence of different emissive centers. This result might be explained by the previously evoked structural problem and the presence of oligomer inter-chain interactions.



Scheme 3 The mechanism of solvent attack side reaction

Finally, the thermal study revealed that the obtained oligomer underwent a twostep degradation most probably corresponding to the decomposition of the pendant chains and the conjugated backbone, successively. However, the oligomer presented a satisfactory thermal stability for use in opto-electronic devices.

Conclusions

In this paper, the electrochemical behaviour of a substituted chalcone, the 4,4'dimethoxychalcone (DMC), was investigated by cyclic voltammetry and potential imposed electrolyses in acetonitrile at a platinum working electrode. This study showed that, at the analytical scale, the coupling of the radical cations, issued from the first electron transfer, was the governing reaction near the electrode. The preparative scale electrolyses led to a di-substituted oligo-phenylene vinylene. The obtained material was characterized by different physico-chemicals methods. The primary optical study confirmed the semi-conducting character of the obtained material with an optical and an electrochemical bandgap of 3.15 and 2.86 eV, respectively. On the basis of the obtained results, a mechanism describing the radical cation evolution toward oligomer formation was evoked. This work described a new electrochemical reactivity of a methoxy-substituted chalcone affording an original route for the preparation of an organic semi-conducting material. In a future work, other substituted chalcones will be studied to test the generalization of this synthetic method.

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