Electrodeposition of 4, 4'-di-*tert*-butylbiphenylperoxide from the anodic oxidation of *p-tert*-butylphenol in an alkaline acetonitrile solution

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Abstract

The electrogeneration of pure 4,4'-di-*tert*-butyl biphenyl peroxide as an electrodeposit could be achieved on a platinum electrode through the anodic oxidation of *p-tert* butylphenol in the presence of Lutidine, in addition to several soluble oligomers. The electrochemical and theoretical studies have shown that the favored coupling reaction corresponds to the O-O bond, albeit it is generally being considered unstable. Without the strong base, a mixture of trimer, tetramer and pentamer was deposited. The peroxide product presents a different electroactivity to that of the phenolic compound, with the appearance of a redox process involving cathodic and anodic symmetrical peaks at -0.10/ 0.15 V vs SCE, which indicates the preference of the polymer to adhere onto the electrode surface. The thermal degradation has also been analyzed. Quantum-chemical calculations reveal the reason for the oxygen-oxygen coupling.

Keywords: *P-tert*-butyl phenol; Electrolysis; Cyclic voltammetry; Electrodeposit; Peroxide dimer.

1. Introduction

Organic peroxides are interesting compounds that play an important role as initiators of polymerization in cement dents and pharmaceutical drugs [1-3]. The use of benzoyl peroxide as oxidant results in a highly pure polyaniline salt [4]. The polymerization of diethyl vinylphosphonate and diisopropyl vinylphosphonate was performed with a high yield in the presence of tertbutylperoxide as the initiator [5].

Numerous studies have focused in the preparation of organic peroxides through the reaction of hydrogen peroxide with the monoketone, diketone and triketone carbonyl groups [6-9]. When reacting hydrogen peroxide with 3-acetylpentane-2,4-dione, tricyclic material containing three peroxide groups was obtained [10, 11]. Other methods are also described in the literature for the synthesis of peroxides. Some of them have followed the direct dioxygenation [12]. There is also another method based on the addition of nucleophilic alkene to peroxycarbenium ions derived from monoperoxy ketal [13]. However, up to now the electrochemical synthesis of peroxides has never received attention.

Controlling the electrochemical pathway and the electrodeposition process are two goals which have attracted much interest in the field of electrochemistry and which are believed to be reached by choosing the appropriate experimental conditions. An interesting example is the anodic oxidation of the phenolic compounds with which the mechanism is generally initiated through the electroformation of phenoxy, phenoxide and phenoxinium [14-16], which are generated by a series of proton and electron transfer reactions [14, 15, 18]. The occurrence of one process or another strongly depends on the medium [19-24]. It has been reported that in acidic conditions, the C-C bond formation is a favored coupling pathway for phenol [19]. By contrast, C-O-C coupling prevails in alkaline solutions [20]. The formation of quinone and acid-catalyzed dealkylation could be avoided in a buffered solution [25]. For the anodic oxidation of 2,6-di-*tert*-butyl-4-methyl phenol, a quinone-methide dimer is obtained in acetonitrile solution, while its corresponding dienone has been found to be the main oxidation product in

an acetonitrile/methanol mixture used as a solvent system [26]. In ionic liquids and in a mixture of methanol and chloroform, the anodic oxidation of 2,6-di-*tert*-butylphenol leads to diphenoquinone and biphenol as major products [27].

2, 6-dimethylpyridine (Lutidine) is a convenient strong base to use for either a proton removal or an attack of a nucleophile on an oxidized substrate   The electrochemical oxidation of 2,4,6-tri-*tert*-butylphenol in acetonitrile as well as in alkaline ethanol produces phenoxide and phenoxy radicals. However, their oxidation produces a phenoxonium ion and ultimately hydroxydienone by water attack [15]. The substituents of the initial substrate and their position provide selectivity regarding the coupled chemical steps. In the case of the non-substituted para-position, the major dimer is formed through para-para linkage [28]. Due to the stabilization of the radicals formed by a positive mesomeric effect of the phenoxide, the anodic oligomerization of phenols with free ortho or para positions leads to ortho/ or para substituted oligomers [21, 29-35]. For 1,3-dihydroxybenzene and 1,4-dihydroxybenzene [36], the predominant dimers are formed through carbon-carbon and carbon-oxygen-carbon links, respectively. By contrast, the peroxide dimer has been qualified as highly unstable since the O-O bond is characterized by the lowest energy dissociation [31, 37]. Nevertheless, the electrosynthesis of such compounds might present an opportunity for the development of free-radical-initiated polymerization [1], especially if they are produced as electrodeposits with high purity. Modified electrodes have been reported upon the anodic oxidation of tyrosine, resveratrol and quercetin [38-40], as well as the oxidation of 2,6-dimethylphenol, 2,4,6-trimethylphenol and 4-*tert*-butylphenol [41], for which the coated films correspond to Poly(phenylene oxide).

In our previous study, the unexpected role of water in the catalysis of the electrooligomerization of *p-tert* butyl anisole was reported [40,41]. In the present work our goal is to investigate the effect of Lutidine on the electrochemical conversion of *p-tert*-butylphenol and the electrosynthesis of its unexpected peroxide dimer with a low thermal decomposition

temperature. In addition, density functional theoretical calculations are performed to underline the reasons of the electrogenation of these kinds of organic compounds which have generally been qualified as not being evident.

2. Experimental

2.1. Chemicals and reagent

Polarographic grade acetonitrile (ACN) and 2,6-lutidine (Lutidine) were purchased from Acros. Dry acetonitrile was obtained through a three-step procedure [44]. After refluxing over $AlCl_3$, distilling, refluxing Li_2CO_3 and redistilling, a further reflux over CaH_2 was achieved under argon. The middle portion of the fractional distillation was used under the same inert atmosphere. Tetrabutyl ammonium perchlorate (TBAP) was purchased from Fluka and was recrystallized before using it as a supporting electrolyte. *P-tert*-butylphenol (**1**) was purchased from Acros and was used without any modification.

2.2. Products

4, 4'-di-*tert*-butylbiphenyl peroxide (**2**): An acetonitrile solution of **1** (1 g, 133 mM) in the presence of Lutidine (0.72 g, 133 mM) was electrolyzed under an argon atmosphere at a potential of 1.8 V vs SCE in a divided cell. The potentiostatic electrolysis was stopped after the consumption of one electron per starting molecule, leading to the electrodeposition of **2** (0.08 g, yield = 8.8%). In addition, *p-tert* butyl phenol dimer, trimer, tetramer and pentamer were detected in the electrolyzed solution by an LC-MS analysis. The yield of **2** was calculated as the ratio of $m_2 / m_{initial\ substrate}$.

2: TLC (SiO_2, eluent n-hexane -dichlorometane1/3 v/v) Rf = 0.46. Retention time in LC-MS: 33.43 min; m/z (relative intensity): 297.64 ($M-H^+$), 298.99 (M^+), 595.78 ($2M-H^+$). Anal.Calcd

for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78; O, 10.72; Found: C, 80.44; H, 9.02; O, 10.54 %. ^{1}HNMR (CDCl$_3$, 300MHz), δ (ppm): 1.31 (1s, 18H, t-Bu), 6.85 (d, 4H, j$_o$= 8.5Hz), 7.25 (d, 4H, j$_o$= 8.5). IR, υ (cm^{-1}): 843, 885, 1270, 1401, 1487, 1618, 1683, 2887, 2975.

2.2. Apparatus and procedure

2.2.1. Electrochemical study

A three-electrode cell with compartments separated by a porous glass was used for the cyclic voltammetry study (Fig.1). The working electrode was a platinum disk (ϕ= 2 mm, EDI type Radiometer) and the counter electrode was a platinum wire. The reference electrode (Saturated Calomel Electrode, SCE) was separated from the bulk solution by a sintered-glass bridge filled with the solvent and the supporting electrolyte. Before each measurement, the working electrode was polished with a set of fine alumina powders.

The macroscale electrolysis at a controlled potential of *p-tert*-butylphenol was carried out in an acetonitrile solution under different conditions. Two platinum grids were used as the working and auxiliary electrodes with a surface area of 6 cm^2 and 3 cm^2, respectively. Bulk electrolysis and cyclic voltammetry were performed with an AUTOLAB PGSTAT 30 potentiostat controlled by the GPES software, version 4.8 (Eco-Chemie, Utrcht, Netherlands). All the potentials obtained are quoted with respect to SCE.

2.2.2. Spectroscopic analyses

^{1}H NMR analyses were made with a Bruker 300 MHz spectrophotometer. An HP 6890 gas chromatograph, HP 5973 mass spectrometer and Auto spec Ultima were used. FTIR-ATR characterizations were performed with a Bruker IFS 66 NS spectrometer. LC-ESI-MS was performed using a Hewlett-Packard 1100 reverse phase high performance liquid chromatography system with a C18 column, hp 1100 series diode array UV-visible detector

(200-400 nm) and series mass analyzer. The mobile phase consisted of an acetonitrile solution + HCOOH (0.1 %). The morphology of the deposited films was examined using a binocular microscope (Leica MZ$_{16}$) fitted onto a camera (moticom 352). XPS spectra were recorded with a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatized Mg-Ka (1253.6 eV) radiation source of 300 W and a hemispheric electron analyzer equipped with nine channeltron electron multipliers. The pressure of the analysis chamber during the scans was about 5×10^{-7} Nm^{-2}. After the survey, spectra were obtained and higher resolution scans were performed at a pass energy of 50 eV. The intensities of the different contributions were obtained by integrating each peak after eliminating the S-shaped baselines and adjusting the experimental curves to a combination of Lorentz (30%) and Gaussian (70%) lines. All the binding energies were compared to the line of the C 1s to 284.4 eV, obtaining values with a precision of ± 0.2 eV. The elemental analysis was made using a Carlo Erba EA1108 device equipped with an auto sampler. The TG -DTA was carried out using a METTLER TOLEDO (model: TGA / SDTA851e / LF / 1600) under a helium atmosphere at 10 °C min^{-1}, with a 3.2 mg sample placed in an open platinum crucible and heated from room temperature to 900 °C. An empty crucible was used as reference.

2.2.3. Computational details

As a preliminary step, the potential energy surface of **1** was studied in the gas phase at the B3LYP/6-31+G(d) level [45] in order to locate the minimum energy. In addition, the optimized structure was reoptimized in an acetonitrile solution using the polarized continuum model (PCM) [46-47]. The unpaired electron spin density analysis was performed at the B3LYP/6-311++G(2df,2p) level. All calculations were carried out with the Gaussian 09 program [48, 49].

3. Results

3.1. Cyclic voltammetry

Figure 1 shows the voltammograms obtained for the p-tert-butylphenol in a dry acetonitrile + 0.1 M TBAP solution at three different positive potential limits. The voltammogram of *p-tert*-butylphenol exhibits three irreversible oxidation waves during the positive-moving sweep (A_1, A_2, A_3) at about 1.28, 1.60 and 2.00 V (Fig.1a), respectively. During the reverse scan, two reduction peaks were observed at 0.45 V (CII) and 0.15 V (CI), respectively (Fig.1b-d); they were observed separately even in the short potential range and when high scan rates were performed (0.25 and 0.50 V s^{-1}). This leads us to presume the occurrence of coupled homogeneous reactions before the scan is reversed, leading to the formation of new oxidation products that are reducible in a more cathodic region than that of the initial oxidation step, A_1. Comparing the amplitude waves of A_1, A_2 and A_3 to that of the anodic wave of ferrocene as reference compound exhibiting one electron transfer in the same voltammetric conditions (Fig.1 e), it is concluded that one electron transfer could be assigned to A_1, A_2 and A_3 which show much lower amplitudes than those in the first step. They also exhibit gradual changes with the increase in the *p-tert*-butylphenol concentration and the decrease in scan rate, consisting in the appearance of several supplementary very low anodic/cathodic systems (Fig.1 f). Such behavior is quite similar to that observed in the case of *p-tert*-butylanisole [41, 42]. This has been attributed to the formation of the corresponding oligomeric products and to a surface phenomenon. In the cathodic scanning, only two small and irreversible cathodic waves appear at about 0.40 (C_I) and 0.10 V (C_{II}). The former shows an important decrease in magnitude when the potential is scanned up until A_1 (Fig.1b-d), suggesting that this electron transfer is related to the reduction of electroactive species electrogenerated in A_2 as well as in A_3. Furthermore, there is no evidence of the electrogeneration of quinone when reduction is observed at about -0.25 V vs SCE [15, 50].

In our previous study about the anodic oligomerization of *p-tert*-butylanisole, an unexpected catalytic effect of water was revealed [42]. A similar effect is also observed regarding the oxidation of *p-tert*-butylphenol (Fig. 2), with the appearance of several redox processes (S$_1$, S$_2$, S$_3$ ..), in the potential range of A$_2$ and A$_3$. At high concentrations, the anodic waves of **1** become increasingly wide until they overlap, while a cross-over phenomenon and loss of reproducibility have previously been observed in the case of aryl ether [41].

In the presence of Lutidine ([Lut]/[**1**]= 0.5), a new and large anodic wave appears at around 0.6 V with an oxidation peak at 1.00 V (As in Fig.3). This process could be assigned to the oxidation of the phenoxide anion, formed after the chemical deprotonation of the phenolic compound, which is more easily oxidized than the initial substrate [15]. In addition, a broad wave appears shifted towards potentials higher than A$_1$ and that might correspond to the successive ejection of electrons by the phenolic compound and the intermediate radical formed in A$_s$. With the increase of Lutidine, the additional peak (A$_S$) appears as a plateau, while a rapidly increasing current is observed in a more positive potential region than that of **1**, leading to a thinner peak at 1.68 V with a concentration ratio of about 1. However, the magnitude of each of these two anodic waves corresponds to only half the magnitude of A$_1$, which could be a sign of a fairly rapid generation of oligomers undergoing a further oxidation in these potential fields. When this ratio reaches 1.5, the voltammogram exhibits two cross over phenomena located between A$_s$ and A$_1$ which could indicate the appearance of some complications in the electrode surface, such as the growth of a new phase.

For A$_1$, an anodic displacement is observed when the scan rate is increased in dry and wet acetonitrile (0.01 % H$_2$O), leading to linear variations of $E_{A_1}^p$ with logv, with slopes > 200 mV decade^{-1}. This result agrees well with a very slow electron ejection from **1** and tends towards an ECE mechanism, which is well established for the electrochemical oxidation of the phenolic

compounds, generally initiated by the generation of several cation and radical cation intermediates [14-16, 51].

3.2. Macroscale electrolysis

Regarding macroscale electrolysis, the focus was set on the effect of the presence of Lutidine on the effective electrochemical conversion of **1** by means of potentiostatic electrolysis. Several experiments were carried out in a separated cell, in which the working electrode is separated from the auxiliary electrode, and in non-separated cells (Figs.4 and 5) at different substrate concentrations and imposed potentials. However, the most relevant results indicate the electrodeposition of two kinds of electrodeposits, which is strongly dependent on the presence or the lack of the strong base in the electrolysis solution. In Table 1, two of the electrolysis events that provided the highest yields for the deposits of **1** have been illustrated, El_1 ([lut]=0) and El_2 ([Lut]/[1]=1) occurring in separated cells at [1] = 0.133 mol dm^{-3} and under an imposed potential of 1.8 V, close to that of A_1 and that of A_s, respectively. The homogeneity of the solutions was ensured by mechanical stirring. In order to track the evolution of the voltammograms of the electrolyzed solutions, El_1 and El_2 were temporarily interrupted after the consumption of several electrons per molecule of the phenolic compound. After passing 1 F mol^{-1}, a thin layer chromatography analysis of both electrolyzed solutions in silica gel, with a mixture of dichlorometane-hexane (1:1/2 (V/V)) as eluent, revealed the presence of several soluble oxidation products (>7) along with the starting material which is detected even after a prolonged electrolysis. Insoluble oxidation products were also obtained as precipitates and on the working grids. The electrodeposit obtained in the absence of Lutidine was of a brownish color, whereas the one obtained in the presence of the strong base was of a bright orange color. Both electrodeposit films were thoroughly washed with acetonitrile to remove the excess electrolysis solutions and were then dissolved in acetone. The solvent was removed under

vacuum and the products were dried in an oven for 48 hours. The LC-ESI-MS characterization of the oxidation product electrodeposited in the absence of Lutidine in an acetonitrile solvent revealed three signals at 13.42, 15.21 and 18.76 related to an m/z of 446.00 ($M_{Trimer}-H^+$), 594.09 ($M_{Tetramer}-H^+$) and 742.31 ($M_{Pentamer}-H^+$), respectively. For the second deposit, only one signal was detected at a retention time of 33.43 min. This corresponds to an m/z of 297.41 ($M_{dimer}-H^+$), revealing that the obtained film on the platinum grid is with formed with only the compound **2**. However, the analysis of the two electrolyzed solutions indicates the presence of the first seven oligomers of *p-tert*-butyl phenol in addition to the remaining initial substrate. Nevertheless, in both experiments there is no evidence of the chromatographic signal of **2**. It can be seen in Table 1 that the highest yield for the deposit is obtained in the basic medium. These results indicate that the electrodeposition of **2** happens immediately after its electrogeneration, while the El_1 coating is formed after some time.

3.2.1. *Voltammetric study of the electrolyzed solutions*

With the progression of El_1, the evolution of the recorded cyclic voltammograms of **1** is quite similar to that previously reported for *p-tert* butyl anisole [43], especially concerning the emergence of a shoulder in A_1 during the first potential sweep (0.53 F mol^{-1}), as well as a rather large wave (1.00 F mol^{-1}) which disappears during the subsequent cycles (Fig.4a). As for the aryl ether analogue, the platinum surface is covered by a relatively thin electroactive deposit which exhibits several and successive irreversible oxidation waves at 0.20, 0.8, 1.2, 1.35 and 1.8 V (Fig.4b).

In the case of El_2, which was carried out in the presence of Lutidine, the resulting curves, after electricity passes through the electrolyzed solution, show an important anodic wave as well as a cross-over phenomenon. At a consumption of 1 F mol^{-1}, for example, instead of A_s, a wide anodic step appears between 0.9 and 1.9 V (Fig. 5a). In addition, an intersection of the anodic

and cathodic branches of the voltammogram is seen at 1.10 V vs SCE. Under this condition, the oxidation of the deprotonated substrate by a base leads to a surface phenomenon, which could be due to the formation of a film.The platinum undergoes a significant modification when it is covered by a deposit (Fig. 5b) less uniform than that obtained in the experiment without Lutidine, and it exhibits only two irreversible oxidation waves at 0.70 and 1.2 V.

3.2.2. Spectroscopic characterization of 2

In the ^{1}H NMR spectrum of **2 (Fig.6)**, the presence of one singlet at 1.31 ppm and two doublets (J_o) at 6.85 and 7.25 ppm allows us to identify the oxidation product **2** as 4,4'-di-tert-butyl biphenyl peroxide. Fig. 7 shows the FTIR spectrum which confirms this proposed structure. As expected, there is no evidence of the hydroxyl vibration band observed in the case of the phenolic parent compound at 3200 cm^{-1}, while a new band corresponding to the O-O vibration is observed at 824 cm^{-1} [53].

XPS characterization was performed to confirm the structure of the peroxide (Fig. 8). C1s and O1s signals were revealed. The first one was deconvoluted into four distinct peaks at 284.59, 291.17, 285.81 and 287.74 eV. The first two are assigned to aromatic carbons, while the other two are contributions of carbons linked to oxygen [53, 54].

The O1s signal can be fitted to two contributions, those at 531.82 and 533.28 eV, which could be assigned to oxygen-oxygen bridging [55] and a C-O linkage [54], respectively.

3.2.3. Thermal behavior of 2

The thermal stability of **2** was studied with a thermogravimetric analysis (TG-DTG) in an argon atmosphere from room temperature to 900 °C. From Fig. 9, it can be observed that the oxidation product is stable up to 111 °C. Above this temperature, an initial weight loss of approximately 11 wt% is observed, which is in good agreement with the results expected for the evolution of

two oxygen atoms with a theoretical variation of 10.74 wt %. As it has been previously reported for Lauroyl peroxide, a thermal cleavage of O-O peroxide bonds could be considered before melting [1]. The second and third thermal decomposition is located very close within the 250 - 823 K temperature range and; they correspond to an important weight loss of 72 wt%, which could be due to the decomposition of the remaining part of **2**. This compound shows an efficient decomposition such as Benzoyl peroxide, Lauroyl peroxide, methyl ethyl ketone peroxide and *tert*-butyl peroxybenzoate [1]. By contrast, 4,4' *tert*-butyl bisphenyl peroxide presents a lower stability when compared to tert-butyl peroxide which is stable up to 300 °C. Then, according to this thermal decomposition, our peroxide product could be beneficially used as an initiator of polymerization.

3.2.4. Voltammetric study of 2

Just like the phenolic compound, its corresponding oxidation product **2** shows an irreversible anodic wave at approximately 1.25 V ((a) in Fig. 10). Nevertheless, this peroxide compound displays an additional cathodic/anodic system at - 0.15/ 0.10 V (c'/a'). This couple is observed separately over a short potential range. The symmetry of its peaks is consistent with the reduction and oxidation of **2** adsorbed onto the electrode surface. Said peaks occur independently from the oxidation at the anodic wave (a).

4. Discussion and calculations

Potentiostatic electrolysis of *p-tert*-butylphenol in the presence of Lutidine at a potential which is more anodic than A_1 leads to the covering of the working grid by its corresponding peroxide dimer, in addition to several soluble oligomers and insoluble products. By contrast, only its trimer, tetramer and pentamer have been detected in the absence of this strong base. Given that

there is no evidence of the presence of the peroxide in the electrolyzed solution, it is clear that the electrodeposition process of the peroxide occurs immediately after its electrogeneration.

Under basic conditions, the resulting phenoxide anion of **1,** deprotonated by Lutidine, undergoes an initial oxidation proces of one electron in A_s, leading to its corresponding phenoxy radical (**1**$^{•}$). This intermediate probably dimerizes at the oxygen position. This results are in agreement with the B3LYP calculations that show that the highest value of the local spin densities of **1**$^{•}$ is located on the oxygen atom (O9 in Fig. 10 and Table 2).

On this atom, the spin density value is equal to 0.36, while those on C2, C4 and C6 are equal to 0.33, 0.25 and 0.22, respectively. This theoretical result agrees well with the O-O coupling of two radicals of **1** (Scheme 1), as is expected from the spectroscopic characterization of the El_2 deposit. However, the coupled chemical reaction of **1**$^{•}$ has several other pathways, among them a C4-C4 coupling reaction which would lead to the electrogeneration of a mixture of oligomeric products.

Conclusion

The present study describes the electrochemical generation of an unexpected peroxide dimer which is frequently described as an unstable oxidation product. Despite the quite low yields achieved, it was obtained in a pure state as a thin film through an electrodeposition process on a platinum grid, during the macroscale electrolysis of p-tert butylphenol in divided cell, which leads also to several soluble and insoluble oligomers in the cell. Given its thermal instability, it could potentially be used as an initiator in the polymerization process. For this reason, improving the film formation efficiency is one of the issues that remain to be solved.

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