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# Infrared and UV–vis spectra of phenoxonium cations produced during the oxidation of phenols with structures similar to vitamin E

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#### ABSTRACT

Several phenols with structures similar to vitamin E were oxidised and the intermediate species produced were characterised by in situ infrared and UV–vis spectroscopies. The Fourier transform infrared (FTIR) measurements were performed by chemically oxidising the phenols with 2 mol equiv. of NO<sup>+</sup>SbF<sub>6</sub><sup>-</sup> in CH<sub>3</sub>CN and recording the spectra between 1900 and 1300 cm<sup>-1</sup> with an attenuated total reflectance (ATR) probe utilising a fiber conduit and a diamond composite sensor. The compounds that formed long-lived phenoxonium cations displayed two IR absorbances at 1665 (±15) cm<sup>-1</sup> and one at 1600 (±10) cm<sup>-1</sup> associated with the carbonyl, symmetric ring stretch and asymmetric ring stretch modes. The paraquinones are one of the long-term products of oxidation of the phenols, and displayed solution phase IR absorbances at 1650 (±10) cm<sup>-1</sup>. In situ electrochemical UV–vis experiments performed during the oxidation of the phenols led to the detection of bands due to the phenoxonium cations at 295 (±5) and 440 (±15) nm and due to the para-quinones at 260 (±10) nm. The concentration of the substrate and the water content of the solvent had a major effect on the yields of the intermediates and products that were produced during the oxidation reactions.

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#### 1. Introduction

Phenolic compounds have an important function in many biological processes; either in a complementary fashion such as acting as antioxidants, or in a negative role such as acting as endocrine disruptive chemicals [1]. In both scenarios the oxidative behaviour of the compounds is important; thus electrochemical studies have been used extensively to study and characterise the oxidation reactions [2–5]. The initial electrochemical oxidation of phenols can be considered to occur through a series of electron transfer and proton transfer reactions that can be represented in a "square-scheme" mechanism, with the lifetimes of the oxidised compounds varying considerably depending on the structure of the phenol [4,5].

The tocopherols are a series of naturally occurring phenolic compounds consisting of several structurally related forms ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) that differ in the degree of methylation of the aromatic ring. It has been found that  $\alpha$ -tocopherol (the most methylated tocopherol), undergoes an electrochemical ECE oxidation process ( $-2e^{-}/-H^{+}$ ) to form a phenoxonium cation (PO<sup>+</sup>), which is surprisingly long-lived in acetonitrile and dichloromethane solutions (Scheme 1) [6–16]. The reaction is chemically reversible on the milliseconds and hours time-scales, providing the moisture content of the solvent is low, and the phenol can be regenerated in 100% yield [8,9]. The phenoxonium cations of the other forms of the tocopherols have lifetimes considerably less than the phenoxonium cation of  $\alpha$ -tocopherol [10]. In addition to  $\alpha$ -tocopherol, there are presently only a few examples of compounds that are known to form long-lived phenoxonium cations [13,17–21], so it is interesting that one derived from a natural compound ( $\alpha$ -tocopherol) is long-lived, which has led to speculation that it may have some biological importance [10,12].

A recent electrochemical study examined a number of phenolic compounds (POH) with structures similar to  $\alpha$ -tocopherol and identified several compounds whose associated phenoxonium cations survived for at least several minutes in acetonitrile solutions at room temperature [13]. It was proposed (based on processes detected during voltammetric and electrolysis experiments) that the phenoxonium cations (PO<sup>+</sup>) reacted with water in the solvent to form para-quinone hemiketals (Q(OH)), which in some cases could also be electrochemically reduced back to the parent phenols, or reacted further to form the para-quinones (Q) (Scheme 1).

The aim of this study is to provide spectroscopic characterisation of the phenoxonium cations, that can only be usually produced as very short-lived species during flash photolysis experiments in aqueous solutions [22–29]. Under transient conditions the identity of intermediate species can be difficult to determine, thus characteristic spectroscopic data from compounds with relatively long lifetimes can be useful in identifying compounds under conditions where they are likely to be considerably more reactive

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**Scheme 1.** General oxidation mechanism for the phenols.  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$  = H or Me.  $R_5$  = H, Me, CH<sub>2</sub>OH, OMe, OEt, CO<sub>2</sub>Et, or CHCH<sub>2</sub>. n = 1 or 2 [13].

(such as in biological conditions or in aqueous environments). A range of phenols were selected based on previous electrochemical experiments which indicated they formed long-lived phenoxonium cations upon oxidation in acetonitrile (Scheme 2, compounds **1a**, **2a**, **3a**, **4a**, **6a**, **7a**) [6–16]. For comparison purposes, the longterm para-quinone oxidation products of two of the phenols (**1d** and **7d**) were examined, in addition to one compound (**5a**) that was thought to form the para-quinone hemiketal upon oxidation [13].

#### 2. Experimental

HPLC grade  $CH_3CN$  (Tedia) was dried over 3 Å molecular sieves and  $Bu_4NPF_6$  was prepared and purified by standard methods [30]. NOSbF<sub>6</sub> (99%) used for chemical oxidation experiments was obtained from Sigma–Aldrich. The synthesis of the phenols and quinones used for analysis has been described previously (Scheme 2) [13,31].

Cyclic voltammetric (CV) experiments were conducted with a computer controlled Eco Chemie Autolab PGSTAT 100 with an ADC fast scan generator. Working electrodes were 1 mm diameter planar Pt disks, used in conjunction with a Pt auxiliary electrode and an Ag wire reference electrode connected to the test solution via a salt bridge containing  $0.5 \text{ M Bu}_4\text{NPF}_6$  in CH<sub>3</sub>CN. Accurate potentials were obtained using ferrocene as an internal standard that was added to the test solution at the end of the measurements. Bulk oxidation experiments were performed in a divided controlled potential electrolysis (CPE) cell separated with a porosity no. 5 (1.0–1.7  $\mu$ m) sintered glass frit [32].

In situ UV-vis spectra were obtained with a Perkin-Elmer Lambda 750 spectrophotometer in an optically semi-transparent thin layer electrochemical (OSTLE) cell (pathlength = 0.05 cm) using a Pt mesh working electrode [33,34]. UV-vis experiments at 253 K were controlled with a Thermo Electron Neslab RTE 740 circulating bath and a thermostatted cell holder. Solution phase background subtracted in situ FTIR experiments were conducted with a Mettler Toledo iC10 spectrometer utilising a diamond composite ATR fiber conduit probe [35,36].

#### 3. Results and discussion

#### 3.1. Electrochemical mechanism

Scheme 1 shows the general mechanism for the electrochemical oxidation in CH<sub>3</sub>CN or CH<sub>2</sub>Cl<sub>2</sub> of the class of phenols (POH) used in this study that have a five- or six-membered ring containing an ether group, with the ether oxygen in the para-position to the hydroxyl group [13]. In CH<sub>3</sub>CN containing Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte, the electrochemical mechanism is similar for all the compounds and involves the initial one-electron oxidation of POH at approximately +0.5 V vs. Fc/Fc<sup>+</sup> (where Fc = ferrocene) to form the radical cation (POH<sup>+</sup>•). POH<sup>+</sup>• rapidly dissociates via the loss of the hydroxyl proton to form the phenoxyl neutral radical (PO•), which is then immediately further oxidised at the electrode surface by one-electron to form the phenoxonium cation (PO<sup>+</sup>) [13]. A homogeneous disproportion mechanism may alternatively account for the second electron transfer step [16]. Although the expression "phenoxonium" is used to describe the cations, molecular orbital calculations and NMR experiments on the model phenoxonium cation of  $\alpha$ -tocopherol (compound **1b**) indicated that most of the positive charge is located on the carbon atom adjacent to the ether oxygen atom, rather than on the oxygen atom [9].

The lifetime of PO<sup>+</sup> depends on the substituents in the  $R_1-R_5$  positions (Scheme 1), as well as the temperature and solvent composition [13]. Some phenoxonium cations have been found to be long-lived (for at least several minutes) and can be reversibly reduced back to the starting materials. A typical cyclic voltammogram of a compound (**1a**) that forms a phenoxonium ion that



Scheme 2. Structures of starting materials.



**Fig. 1.** Representative cyclic voltammograms recorded at a scan rate of  $100 \text{ mV s}^{-1}$  in CH<sub>3</sub>CN containing 0.2 M Bu<sub>4</sub>NPF<sub>6</sub> for 5 mM of the phenols and related compounds at 22 (±2)°C. (–) Chemically reversible  $-2e^{-}/-H^+$  transformation of phenol (**1a**) into phenoxonium ion. (...) Reduction (+2e<sup>-</sup>/+2H<sup>+</sup>/-H<sub>2</sub>O) of para-quinone hemiketal (**5c**) back to phenol. (---) Chemically reversible +1e<sup>-</sup> transformation of para-quinone (**1d**) into semiquinone. Data modified from reference [13].

survives for at least the voltammetric time-scale (a few seconds) is shown in Fig. 1 (solid line) where a forward oxidation peak  $(E_n^{ox})$  is observed at approximately +0.5 V vs. Fc/Fc<sup>+</sup> and a reverse reduction peak  $(E_p^{red})$  is detected at approximately +0.2 V vs. Fc/Fc<sup>+</sup>. Both the forward and reverse processes correspond to the transfer of twoelectrons and one proton. The wide separation between the  $E_p^{ox}$  and  $E_{\rm p}^{\rm red}$  peaks ( $\Delta E_{\rm pp}$ ) is due to the electron transfer reactions occurring sequentially in two one-electron steps at different potentials, with a proton transfer reaction interspersed between the electron transfers (an ECE mechanism) [8–16]. The voltammograms in Fig. 1 are representative of a general reaction scheme of phenols; however, not all of the processes may be detectable for all compounds. For example, the phenoxonium cations of the majority of phenols are not long-lived, therefore, the peak for the reduction of the phenoxonium back to the phenol at +0.2-+0.4V is seldom observed (especially at slow scan rates).

Most PO<sup>+</sup> compounds react quickly with trace water (or other nucleophiles) in the solvent to form the para-quinone hemiketals (Q(OH)) as a major product, which can convert into the paraquinones (Q), although the reaction is concentration dependant and also involves the formation of other unidentified products (Scheme 1) [13]. Evidence for the para-quinone hemiketal intermediates came from the observation that during electrolysis experiments new species were produced with reductive peaks at approximately -0.4 V vs. Fc/Fc<sup>+</sup> for some of the compounds (such as 5c) (Fig. 1, dotted line). The reduction potential of the intermediate occurred between that observed for the phenoxonium ion (solid line) and that observed for the stable para-quinone (dashed line). Applying a potential more negative than -0.4 V vs. Fc/Fc<sup>+</sup> allowed the intermediate compound be reduced back to the starting material indicating that it was unlikely to be a ring-opened structure such as the para-quinone (which cannot be reduced back to the starting materials under the mild conditions used for electrochemistry), and supporting the formation of the para-quinone hemiketal. The para-quinone hemiketals rearrange slowly in solution into the para-quinones which can be reduced at approximately -1 V vs. Fc/Fc<sup>+</sup> in a one-electron chemically reversible process (such as for 1d) (Fig. 1, dashed line). Experiments on solid state samThe phenoxonium cations can also be prepared in two oneelectron steps, if the reaction is commenced with solutions containing the phenolate anions [3,7,8]. Preparation of the phenolate starting materials requires initial reaction of the phenols with an organic soluble base, such as a tetraalkylammonium hydroxide, which are commercially available as concentrated aqueous solutions and difficult to dry [7]. Therefore, because of the higher amount of water that is present in solutions of the phenolate anions (due to the addition of the base), the phenoxonium cations (which are reactive with water) were prepared directly from the phenol starting materials.

#### 3.2. Infrared spectroscopy

In this study, the phenoxonium cation reaction intermediates were prepared by chemical oxidation of the phenolic starting materials in preference over electrochemical oxidation. It has not been conclusively proven that the identical oxidation pathway occurs for chemical oxidation of the phenols compared to heterogeneous oxidation at solid electrodes [8,10,12], although it is known that chemical oxidation of  $\alpha$ -tocopherol with 2 mol equiv. of NO<sup>+</sup> produces the phenoxonium cation in 100% yield [9,11]. Fig. 2 shows in situ background subtracted ATR–FTIR spectroscopic data that were obtained by chemically oxidising a range of phenols in CH<sub>3</sub>CN



**Fig. 2.** Background subtracted in situ ATR-FTIR spectra obtained by oxidising 0.1 M of the phenols in CH<sub>3</sub>CN with 2 mol equiv. of NOSbF<sub>6</sub> 22 at  $(\pm 2)^{\circ}$ C. The spectra represent 256 scans recorded with 4 cm<sup>-1</sup> resolution. (...) Starting phenols. (–) Immediately after oxidation, except for **1d**, which is a pure compound.

with 2 mol equiv. of NOSbF<sub>6</sub>. The dotted lines in Fig. 2 are the initial spectra of the phenols and the solid lines are the spectra of their associated phenoxonium cations. The phenols in Fig. 2 were chosen based on previous controlled potential electrolysis experiments that indicated that their associated phenoxonium cations had lifetimes of at least several minutes [13]. CH<sub>3</sub>CN is the preferred solvent for the oxidation experiments because it affords the greatest lifetimes of the phenoxonium ions and because it has few bands in the infrared region that interfere with the FTIR detection of the phenoxonium cations. NO<sup>+</sup> was used as the oxidant because the chemical oxidation occurs much more rapidly than electrochemical oxidation, because its reduction potential is sufficiently positive to oxidise many phenols and because it is cleanly reduced to NO(g) which is easily removed from solution [9].

The ATR probe used for the in situ FTIR experiments has a usable range between approximately  $1900-650 \text{ cm}^{-1}$  [35,36], although it is the carbonyl region ( $1800-1600 \text{ cm}^{-1}$ ) that is the most useful in characterising the phenoxonium ions [8–10]. The sensitivity limits of the ATR–FTIR probe require relatively high concentrations of substrates, therefore; all experiments were conducted with 0.1 M concentrations of the phenols. There is presently no evidence to indicate that the short term oxidation mechanism of the phenols to form the phenoxonium cations is concentration dependant [8–16].

The infrared spectra of the oxidised forms of the phenols in Fig. 2 appear similar and show three characteristic bands between 1681 and 1604 cm<sup>-1</sup> (the highest wavenumber band often appearing as a shoulder). Compounds 1b and 2b mainly differ in that they contain a 6-membered heterocyclic ring while compounds 3b and 4b contain a 5-membered heterocyclic ring. Previous molecular orbital calculations on compound **1b** indicated that the structure was indeed similar to that of a quinone (as drawn in Fig. 2), consisting of a carbonyl group and a cyclic diene [9]. Therefore, the infrared region between 1800 and 1500 cm<sup>-1</sup> would expect to show absorbances due to a carbonyl stretch, a symmetric diene ring stretch and an asymmetric diene ring stretch. Nanosecond time resolved resonance Raman spectroscopy in CH<sub>3</sub>CN/H<sub>2</sub>O solutions of a 4-acetoxy-4-aryl-2,5-cyclohexadienone led to the detection of a phenoxonium cation, which displayed a C=O stretch (1635 cm $^{-1}$ ), a symmetric diene ring stretch (1593 cm<sup>-1</sup>) and an asymmetric diene ring stretch (1525 cm<sup>-1</sup>) [28].

Molecular orbital calculations on compound 1b predict that two of the bands are associated with the symmetric and asymmetric ring stretching modes and one band is associated with the carbonyl stretching mode, although in each case other coupled vibrations within the molecules contribute to the modes [9]. The absorbance at close to 1600 cm<sup>-1</sup> is predicted to be associated with the asymmetric ring stretching mode [9]. The two bands that occur at 1663 (which appears as a shoulder) and 1650 cm<sup>-1</sup> (in the spectrum of **1b**) are predicted to be due to the carbonyl stretch and symmetrical ring stretch, respectively [9]. The molecular orbital calculations predict the carbonyl band to be at the higher wavenumber, which, if correct, means that it is weaker in intensity than the symmetric ring stretching mode. Therefore, in the FTIR spectra of all the phenoxonium cations in Fig. 2, the absorbance at the highest wavenumber (which appears as a shoulder in the spectrum of **3b** at 1681 cm<sup>-1</sup>), is likely to be associated with the carbonyl stretching mode. The spectrum of the quinone of the  $\alpha$ -tocopherol model compound (1d) is provided in Fig. 2 as a comparison to the phenoxonium cations, and shows one strong band in the carbonyl region at 1645 cm<sup>-1</sup>, possibly because the C=O stretch and symmetric ring stretching modes are overlapping.

The spectra of all the phenoxonium cations in Fig. 2 also show a strong absorbance at close to  $1500 \,\mathrm{cm^{-1}}$ , which is the strongest absorbance between 1900 and  $1300 \,\mathrm{cm^{-1}}$ . Molecular orbital calculations on compound **1b** predicted several absorbances close to  $1500 \,\mathrm{cm^{-1}}$  that coincide with the C–O stretch coupled with bend-



**Fig. 3.** Background subtracted in situ ATR-FTIR spectra obtained by oxidising 0.1 M **5a** in CH<sub>3</sub>CN with 2 mol equiv. of NOSbF<sub>6</sub> 22 at  $(\pm 2)^{\circ}$ C. The spectra represent 256 scans recorded with 4 cm<sup>-1</sup> resolution (...) **5a**. (–) The spectrum of **5b** was obtained immediately after oxidation and the spectrum of **5c** was obtained from **5b** after the addition of 0.1 M of water.

ing modes of the methyl groups on the quaternary carbon [9]. The C–O stretching modes in ethers normally occur between 1300 and 1000 cm<sup>-1</sup> [37]. Nevertheless, an X-ray crystallographic study on compound **1b** showed that the quinoid like carbon–oxygen ether bond in the phenoxonium cation is shorter than a normal C–O bond [11], which could account for the shift in the absorbance of the C–O bond to higher wavenumbers in the cation.

The lifetime of the phenoxonium cations is partly determined by how reactive they are with nucleophiles, such as water, in the solvent [10]. In an ultra-dry environment it has been found that the phenoxonium cation of the model compound of  $\alpha$ -tocopherol (**1b**) can survive for at least several weeks at  $-27 \degree C$  [9,11]. Since water is always present in organic solvents, the phenoxonium cations may be longer lived at higher concentrations where the effects of trace water are less, providing they do not react in a dimerisation or related processes. The water concentration of the CH<sub>3</sub>CN inside the reaction vessel was calculated to be  $25 (\pm 5) \text{ mM}$ , based on the published experimental procedure where values of  $|E_1 - E_2|$  for a quinone are correlated with the amount of water present ( $E_1$  and  $E_2$ are the first and second reduction potentials of vitamin  $K_1$  [38,39]. The high humidity of the local environment combined with the cell used for the in situ spectroscopic analysis make it difficult to completely exclude the water from the solvent.

Fig 3 shows infrared spectra that were obtained before and after the oxidation of compound **5a** with 2 mol equiv. of NO<sup>+</sup>. The spectrum obtained immediately after the oxidation of 5a showed absorbances in the carbonyl region typical of the phenoxonium cation at 1660 (shoulder), 1651 and 1605 cm<sup>-1</sup>, and with a strong absorbance close to 1500 cm<sup>-1</sup>. The phenoxonium cation of compound 5a (5b) is known to be more reactive with water than compounds 1b-4b [13], thus when an equal molar amount of water was added to the solution, the spectrum of **5b** immediately diminished in intensity to most likely form 5c (the para-quinone hemiketal) (Fig. 3). There are several reports on the existence of para-quinone hemiketals related to the tocopherols, although the compounds are difficult to obtain in pure form and rapidly convert in the presence of acid to the quinones [31,40–44]. The infrared stretching frequency of the carbonyl group of the para-quinone hemiketals of the tocopherols have been assigned between 1680 and  $1630 \, \text{cm}^{-1}$  [40–44], although there is some ambiguity whether



**Fig. 4.** In situ electrochemical UV–vis spectra obtained in  $CH_3CN$  containing 0.2 M  $Bu_4NPF_6$  during the oxidation of approximately 1 mM of the phenols at -20 °C. (...) Starting phenols. (–) Intermediate scans. (–) Final scan.

this may be a strong ring stretching mode, as is observed in the phenoxonium cations.

The band that was present in the spectrum of **5b** at  $1651 \text{ cm}^{-1}$  appears to shift to  $1647 \text{ cm}^{-1}$  in the spectrum of **5c**. The band at  $1647 \text{ cm}^{-1}$  for **5c** could be due to either a carbonyl stretch or ring stretching mode (or an overlap of both). Although the band at  $1647 \text{ cm}^{-1}$  occurs at a similar wavenumber to that observed for a quinone, such as **1d** in Fig. 2, it is unlikely that **5b** converts so rapidly and quantitatively to the quinone in the presence of an equal molar amount of water. Normally the conversion of phenols to quinones in non-aqueous solvents is a relatively low yield reaction with numerous side products [13,31]. The broad band that occurs at approximately  $1720 \text{ cm}^{-1}$  in the spectrum of **5c** is due to water.

#### 3.3. In situ electrochemical UV-vis spectroscopy

Fig. 4 shows in situ electrochemical UV–vis experiments that were conducted on compounds **1a**, **2a** and **3a** which are known to form relatively long-lived phenoxonium cations [13]. The spectroscopic experiments were performed over a time-scale of around 30 min and needed to be performed at low concentrations (<1 mM) to avoid overloading the instrument detector. There is a disparity in the concentration of the phenolic compounds used in the infrared and UV–vis spectroscopic experiments because of the infrared experiments requiring very high concentrations in order to obtain acceptable signal-to-noise ratios. The low concentration of analytes used for the UV–vis measurements leads to there being a substantially higher ratio of water present that favours the formation of the para-quinone hemiketals or para-quinones over the phenoxonium cations. Nevertheless, the UV–vis spectra obtained during the oxi-

dation of the phenolic compounds shown in Fig. 4 are consistent with the formation of the phenoxonium cations [8–10].

The geometry and shape of platinum mesh electrode inside the flat UV-vis cell is not conducive to obtaining clearly interpretable voltammetric peaks, as is achievable for cyclic voltammetry experiments at planar disk electrodes. Therefore, the applied oxidation potential of the Pt mesh electrode in the OSTLE cell was set by slowly increasing the potential until a positive current of a few µA was first observed, and then applying a further +100 mV past this point, which produced an initial positive current of approximately 100 µA. The oxidation reaction was run until the current decreased to <1 µA, or until the present UV-vis spectrum was identical to the previous UV-vis spectrum. In order to regenerate the starting material, a reducing potential of 0 V was applied to the Pt mesh electrode. It was not possible to collect accurate coulometry data during the UV-vis measurements because only the solution inside the flat portion of the cell underwent exhaustive oxidation, while the bulk of the solution was located outside the flat portion of the cell. Previous bulk controlled potential coulometry experiments on the phenols in a conventional two compartment electrolysis cell [32] confirmed that the oxidation reaction occurs via two-electrons per molecule [13].

At 25 °C the starting phenols showed an absorption band at approximately 295 nm with  $\varepsilon \approx 3000 \,\mathrm{L\,cm^{-1}}$  mol<sup>-1</sup> [45,46]. As the temperature decreased the band narrowed and appeared to split into two closely spaced absorbances that could not be completely resolved at -40°C [8]. During the in situ oxidation of the phenols at -20°C, an intense band was observed at 293-296 nm  $(\varepsilon \approx 11,000 \, \text{L} \, \text{cm}^{-1} \, \text{mol}^{-1})$  and a less intense very broad band at 432–452 nm ( $\varepsilon \approx 700 \, \text{L}\,\text{cm}^{-1} \, \text{mol}^{-1}$ ) (the  $\varepsilon$ -values supersede the previously reported values [10,15]). The spectra are very similar to those obtained of the phenoxonium cations of the  $\alpha$ - and β-tocopherols [10]. In each case the spectrum of the starting material could be completely regenerated by applying a 0V reducing potential to the electrode, indicating that the oxidised compounds were long-lived. Laser flash photolysis of a 4-acetoxy-4-aryl-2,5cyclohexadienone in O<sub>2</sub> saturated CH<sub>3</sub>CN/H<sub>2</sub>O solutions led to the detection of two transient species with absorption bands at 460 and 360 nm [26,28]. The band at 460 nm was assigned to the phenoxonium cation (similar to this work), and the band at 360 nm assigned to a phenoxyl free radical [28]. Under the slower time-scale experiments in this work, any phenoxyl radicals produced are unlikely to be sufficiently long-lived to detect, thus the bands at approximately 300 and 450 nm are both associated with the phenoxonium cations.

Fig. 5 shows the UV-vis spectra obtained during the electrolysis of compounds 4a, 6a and 7a. In this instance, the phenoxonium cations (4b, 6b and 7b), formed by electrochemical oxidation were known to be more reactive than compounds 1b, 2b and 3b [13]. The initial oxidation of the phenols did produce the phenoxonium cations, as evidenced by the initial increase in intensity of the bands at approximately 300 and 436-452 nm. However, as the electrolysis progressed, these bands diminished in intensity again and a strong band (or pair of bands) was detected at 254-264 nm. The band detected at 254-264 nm is very similar to that observed in the UV-vis spectra of the quinones shown in Fig. 6. Therefore, it appears that in the low analyte concentration UV-vis measurements, there is a greater tendency for the oxidised compounds to react to form the quinones (4d, 6d and 7d') as one of the final products, which accounts for the higher apparent reactivity of 4b in the UV-vis measurements compared to in the infrared measurements (in addition, the UV-vis measurement were performed over a longer time-scale allowing more time for a hydrolysis reaction). It was found that the spectra of the starting phenols could not be regenerated by applying a reducing potential after the initial oxidation of compounds 4a, 6a and 7a.



**Fig. 5.** In situ electrochemical UV-vis spectra obtained in CH<sub>3</sub>CN containing 0.2 M Bu<sub>4</sub>NPF<sub>6</sub> during the oxidation of approximately 1 mM of the phenols at -20 °C. (...) Starting phenols. (-) Intermediate scans. (-) Final scan.



Fig. 6. UV-vis spectra of approximately 1 mM of the quinones obtained in CH\_3CN at 22 ( $\pm 2)\,^\circ\text{C}.$ 

The FTIR spectra obtained during the chemical oxidation of **6a** and **7a** at high concentrations with NOSbF<sub>6</sub> were complicated and showed a number of bands in the carbonyl region that were weak in intensity suggesting that a number of products were formed (in addition to the phenoxonium cations or quinones) and were difficult to interpret. Therefore, although Scheme 1 and Fig. 1 represent a general reaction pathway, it is likely that in many cases other reactions can occur making it difficult to fully characterise the FTIR

and UV-vis spectra of the phenoxonium cations, hemiketals and quinones associated with all phenolic compounds.

#### 4. Conclusions

Infrared spectroscopic measurements made during the oxidation of several phenols led to the detection of a range of products depending on the lifetimes of the oxidised compounds. The compounds that formed long-lived phenoxonium cations showed two infrared absorbances between 1685 and 1650 cm<sup>-1</sup> (sometimes overlapping into one band) due to the carbonyl stretching and symmetric ring stretching modes and a band at approximately 1600 cm<sup>-1</sup> due to the asymmetric ring stretching mode. The phenoxonium cations also showed a very intense band at approximately 1500 cm<sup>-1</sup>, which is possibly associated with a C-O single bond mode(s). The solution phase spectra of the ring-opened quinones showed a single strong infrared band in the carbonyl region at approximately 1650 cm<sup>-1</sup>. The UV-vis spectra of phenoxonium cations showed intense bands at 293-296 nm and relatively less intense bands at 434-460 nm, compared to the long-term paraquinone oxidation products that showed bands at 256-264 nm.

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