

Electrogenerated HO radical reactions: the role of competing reactions on the degradation kinetics of hydroxy-containing aromatic compounds

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Abstract

The rate of degradation of some aromatic compounds, benzoic acid, 2-hydroxybenzoic acid, 4-hydroxybenzoic acid and 2,3-hydroxybenzoic acid, by electrogenerated HO radicals is investigated. The effect of the addition of secondary species, that can either be a reaction product of the target compound or not is analysed. The presence of the actual reaction products is also considered. The action of these secondary species is integrated in a general model that accounts for the dependency of the anode coverage by HO radicals on the concentration and on the reactivity of HO radical scavengers. From the magnitude of the effect of competing reactions, the reactivity of the hydroxybenzoic acid derivatives was estimated as the product between the stoichiometric coefficients and the rate constants. A possible mechanistic interpretation is provided to explain the unexpected high values of the stoichiometric coefficients estimated that largely exceed the number of radicals required for the complete mineralization of the species.

Keywords

1. Introduction

Hydroxyl radical is one of the most powerful oxidant. Although it is best known for its deleterious action against cell components in oxidative stress [1], its application in the destruction of pollutants is particularly valuable regarding environmental friendly technologies [2]. Regardless of the research/ application field, the understanding of HO radical reactions is of great interest.

The generation of HO radicals is carried out in most laboratories by the so-called Fenton or Fenton-type reactions that use metal ions such as Fe(II) or Cu(II) to reduce H_2O_2 [3,4]. Despite the simplicity and accessibility of such methods, alternative ways have been suggested for this purpose, including the sono-Fenton [5], photo-Fenton [6], the electro-Fenton [7,8], sono-electro-Fenton [9] and photo-electro-Fenton [10,11]. Besides, HO radicals can also be generated by the photolysis of H_2O_2 [12] or by sonolysis [13] or radiolysis of water [2,14].

Electrochemical techniques are also used to generate HO radicals. The formation of HO radicals during the electrooxidation of water at different anode materials, such as Pt, IrO_2 , SnO_2 and BDD was demonstrated by the identification of hydroxylated products [15] or using spin traps, as N,N-dimethyl-p-nitrosoaniline [16] or 5,5-dimethyl-1-pyrroline-N-oxide [17]. Besides the well-known advantages of electrochemical techniques, e.g. low cost and easy automation, the extent and rate of oxidation reactions can be controlled by the nature of the anode material. [15,16]. As adsorption strength of electrogenerated HO radicals to BDD (boron doped diamond) anodes is low, quasi-free HO radicals are formed. In opposition to the HO radicals formed at Pt anodes that are, strongly adsorbed [18].

The generation of strongly adsorbed HO radicals can be rather interesting for comparing the reactivity of different species [19] or else for mechanistic studies. As the oxidation tends to be more selective, less reactive intermediaries can be stabilized. This possibility can be exploited in order to identify these intermediaries or to obtain information on secondary or competing reactions.

In the present work we present a kinetic study on the consumption of aromatic compounds that aims to elucidate the role of competing reactions. These reactions can be quite significant as HO radicals are not selective and can react with a given compound and simultaneously with its reaction products. Besides, in natural systems (e.g. biological or wastewater) organic molecules occur in more or less complex mixtures. Therefore competing reactions cannot be avoided.

2. Experimental

2.1. Chemicals

All reagents employed were of analytical grade. Benzoic acid (BA; Prolabo), 2-hydroxybenzoic acid (2-HBA; Vaz Pereira), 4-hydroxybenzoic acid (4-HBA; BDH Chemicals) and 2,3-dihydroxybenzoic acid (2,3-HBA; ACROS Organics). Potassium chloride (Fluka), potassium ferricyanide (José Gomes Santos), potassium dihydrogen phosphate and phosphoric acid (ACROS Organics). Methanol was of HPLC grade from Fisher Scientific. Solutions were prepared in 0.15 M buffer (pH 3.2) containing potassium dihydrogen phosphate and phosphoric acid.

2.2. HPLC

Oxidation reactions were monitored following the concentration decrease along galvanostatic electrolyses by HPLC. HPLC experiments were performed using a

Jasco, PU-2080 Plus system equipped with a RP 18 column from Grace Smart (250 mm × 4.6 mm, 5 μm particle size) and using Clarity HPLC software from Jasco (Jasco 870 / UV detector). A flow rate of 0.6 ml min⁻¹ and a loop of 20 μl were used. A mixture of methanol, water and phosphoric acid (60:39:1) (v/v) was used as mobile phase. The detection wavelength was selected according to species: 210 nm for 2-HBA and 2,3-HBA and 230 nm for BA and 4-HBA. The quantification was performed using calibration curves.

2.3. Electrolysis

Galvanostatic electrolysis were carried out (using a potentiostat Autolab type PGSTAT30, Ecochemie) at 1250 A m⁻² in a two compartments cell separated by a glass frit membrane. Volume of anodic compartment is V = 9.0 ml and solution was mechanically stirred with a magnetic stir bar (300 rpm). Anode is made of a piece (20 mm × 10 mm) of Pt gauze (52 mesh woven from 0.1 mm diameter wire, 99.9%, from Alfa Aesar). Before each experiment the anode was electrochemically cleaned in the phosphate buffer solution pH 3.2 during 600 s at a constant current of 0.02 A. The area of the Pt working electrode (A = 5.6 cm²) was determined in a chronoamperometry experiment using 1.00 mM of K₃[Fe(CN)₆] in 0.1 M KCl [20].

The assessment of apparent rate constants, k_{app} , of the consumption of benzoic acid, 2-hydroxybenzoic acid, 4-hydroxybenzoic acid and 2,3-hydroxybenzoic acid during the galvanostatic electrolysis was performed by the analysis of the concentration decay curves by a first order law ($\ln C/C^0 = -k_{app} A / V t$) [15].

3. Results and discussion

Using Pt anodes fairly oxidized, in conditions where HO radicals are produced by oxidation of water, the consumption of aromatic compounds is not limited by mass transport, but by the kinetics of charge transfer and by the kinetics of reaction with HO radicals [19]. The apparent rate constants of degradation of aromatic compounds, k_{app}^0 , are related to the reactivity of the species, according to eq. 1 and to eq. 2 for non-electroactive and for electroactive compounds, respectively [19].

$$k_{app}^0 = \frac{j}{zF} \left(\frac{1}{\frac{2k_{O_2}}{k_{S,HO}} + n_S[S]} \right) \quad (1)$$

$$k_{app}^0 = \frac{j}{zF} \left(\frac{1}{\frac{2k_{O_2}}{k_{S,HO}} + n_S[S]} \right) + k_{S,e} \quad (2)$$

Where k_{O_2} is the rate constant of the reaction of O₂ evolution (according to eq. A.2, of appendix), $k_{S,HO}$ is the rate constant of the consumption of a species S by reaction with HO radicals adsorbed at the anode surface (according to eq. A.4), n_S is the stoichiometric coefficient, $k_{S,e}$ is the rate constant of the oxidation of S by direct electron transfer, z is the number of electrons involved in the electrogeneration of HO radical, j is the current density of the galvanostatic electrolysis and F is the Faraday constant. The fact that k_{app}^0 is constant during the electrolysis of a number of aromatic compounds, despite the consumption of the compound, it means that the HO surface concentration kept constant during the electrolysis. This evidence was taken as an indicator that $n_S[S]$ would be much smaller than $2k_{O_2} / k_{S,HO}$ (eq. 1 and eq. 2). On the basis of this consideration, values of $k_{S,HO} / k_{O_2}$ were evaluated from the slope of the representation of k_{app}^0 vs j .

Although this approach suited our previous results [15,19] it is not adequate to interpret the new evidences provided by experimental data presented herein regarding

the occurrence of competing reactions. The oxidation of a target compound in the presence of a second species, that can either be a reaction product of the target compound or not is considered in sections 3.1 and 3.2. The effect of the actual reaction products is also analysed (section 3.3) in experiments where the oxidation of a single starting compound is carried out at different initial concentrations, covering two orders of magnitude, so that the concentration of the formed products can also vary significantly.

3.1. Kinetic analysis of benzoic acid reaction with HO radicals in the presence of 2-hydroxybenzoic acid or of 4-hydroxybenzoic acid

The consumption of benzoic acid (BA) by galvanostatic electrolysis along time is displayed in Fig. 1A and 1B. The initial concentration of BA was 0.50 mM in all experiments. Circles correspond to results from solutions containing only BA as the starting compound, whereas triangles correspond to data obtained from solutions where BA is mixed with 2-HBA (Fig. 1A) or with 4-HBA (Fig. 1B). The independent variable τ in Fig. 1 is time normalized for the geometric ratio of the cell V/A .

The solid line adjusted to circles was simulated using eq. A.13 and describes the concentration decay of BA ($C_{BA}^0 = 0.50$ mM) in the absence of any other added organic compound. A value of 2331 mol m^{-3} is assigned to $(2 k_{O_2} + CS) / k_{BA,HO}$ in eq. A.13. The parameter CS , defined by eq. A.14, concerning BA oxidation can be expressed as:

$$CS = n_{BA} k_{BA,HO} [BA] + \sum n_{P_{BA,i}} k_{P_{BA,i},HO} [P_{BA,i}] \quad (3)$$

where $k_{BA,HO}$ is the rate constant of BA reaction with HO radical and n_{BA} is the corresponding stoichiometric coefficient; $P_{BA,i}$ ($i = 1, 2, \dots, n$) is a reaction intermediary or product formed directly from the oxidation of BA or from the oxidation of a BA product, $n_{P_{BA,i}}$ is the stoichiometric coefficient of the reaction of $P_{BA,i}$ with HO radicals which rate constant is $k_{P_{BA,i},HO}$ and $[P_{BA,i}]$ is its concentration.

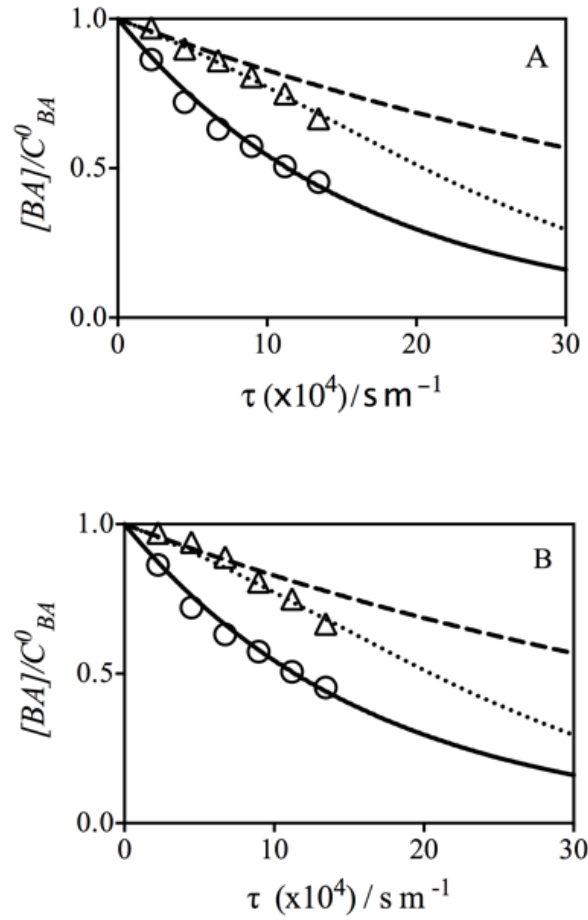


Figure 1. Concentration decrease of BA along time, $C_{BA}^0 = 0.50$ mM, electrolysis conducted at $j = 1250$ A m⁻² alone (O) and in the presence (Δ) of 0.50 mM: 2-HBA (A) or 4-HBA (B). Experimental data are plotted together with simulation curves using: eq. A.13 (solid line), eq. B.8 (dashed line) and eq. B.10 (dotted line). Simulation parameters: $(2 k_{O_2} + CS) / k_{BA,HO} = 2331$ mol m⁻³, $\frac{\overline{n_{2-HBA,P_2-HBA}} k_{2-HBA,P_2-HBA}}{k_{BA,HO}} = 1060$ mol m⁻³, $k_{C(2-HBA,P)} = 3.5 \times 10^{-5}$ m s⁻¹ (A) and $(2 k_{O_2} + CS) / k_{BA,HO} = 2331$ mol m⁻³, $\frac{\overline{n_{4-HBA,P_4-HBA}} k_{4-HBA,P_4-HBA}}{k_{BA,HO}} = 36250$ mol m⁻³, $k_{C(4-HBA,P)} = 5.0 \times 10^{-6}$ m s⁻¹ (B).

The fact that BA consumption is described by a pseudo-first order reaction indicates that k_{app}^0 remains approximately constant along time. Considering eq. A.13 this result can be a consequence of one of the following situations. First, the magnitude of k_{O_2} is much larger than that of CS and even if CS can vary along time, the sum $2k_{O_2} + CS$ keeps constant. On the other hand, if CS is comparable to k_{O_2} , it must remain constant despite the consumption of BA. Considering eq. 3, in order that CS remains constant the decrease of the rate of consumption of HO radicals by reaction with BA (first parcel of eq. 3) must be compensated by the increase of its rate of consumption by reaction with the formed intermediaries or products $P_{BA,i}$ (second parcel of eq. 3). In order to clarify about the importance of reaction products on the availability of HO radicals and therefore on k_{app} , experiments were conducted to quantify the effect of the presence of two hydroxylated products 2-HBA and 4-HBA on the consumption rate of BA. The consumption of benzoic acid from the two mixtures (BA + 2-HBA and BA + 4-HBA) show identical features (Fig. 1) in the sense that the concentration decay is slower than the observed in solutions where BA is the single starting compound and that the concentration decrease does not follow an exponential function. These observations were interpreted considering that the reaction of BA with electrogenerated HO radicals was significantly slowed down due to the competition between both organic compounds towards electrogenerated HO radicals. The fact that k_{app} (the rate constant of BA consumption in the presence of a second organic compound) is lower than k_{app}^0 (rate constant of BA consumption in the absence of any added organic compound) is a direct consequence of the lower concentration of HO radicals in the presence of the two organics that can react with these radicals. Therefore, 2-HBA or 4-HBA provides a kind of protective effect towards the consumption of BA by HO radicals. This protective effect tends to

decrease along time given that the consumption of BA tend to accelerate vis-a-vis the predicted by a constant k_{app} . This is illustrated in Fig. 1 by comparing the dashed with the dotted lines.

These lines are simulated using eq. B.10 (dotted lines) or eq. B.8 (dashed lines) that assumes that the concentration of HO radical at the electrode surface is influenced not only by the presence of the two organic compounds initially present in the solution (BA + 2-HBA or BA + 4-HBA) but also by the products of reaction of these compounds ($P_{BA,i}$ and $P_{2-HBA,i}$, or $P_{BA,i}$). The only difference between the two equations is that in eq. B.8 (dashed lines) k_{app} is kept constant while in eq. B.10 (dotted lines) k_{app} diminishes along time.

In eq. B.8 the initial concentration of the species R (2-HBA or 4-HBA), C_R^0 (C_{2-HBA}^0 or C_{4-HBA}^0), is taken as an measure of the total concentration of the species that are able to react with HO radicals C_R^i (defined by eq. B.4), assuming that the decrease of $[R]$ is compensated by the increase of $[P_{R,i}]$. At short times, $\tau < 1 \times 10^5 \text{ s m}^{-1}$, experimental data are adequately simulated by this equation demonstrating that there was no significant decrease of the total concentration C_{2-HBA}^0 and C_{4-HBA}^0 .

In eq. B.10 it is considered that the total concentration of the species that are able to react with HO radicals decrease with time (by a first order reaction with a rate constant of $k_{C(R,P)}$) (eq. B.5).

The parameters used in the simulation are listed in the legend of Fig. 1 where

$\overline{n_{2-HBA,P_{2-HBA}}} k_{2-HBA,P_{2-HBA}}$ and $\overline{n_{4-HBA,P_{4-HBA}}} k_{4-HBA,P_{4-HBA}}$ are the average values of the product between the stoichiometric coefficients and the rate constants of 2-HBA and 4-HBA respectively.

3.2. Kinetic analysis of 2,3-hydroxybenzoic acid reaction with HO radicals in the presence of 4-hydroxybenzoic acid

Results of concentration decrease of 2,3-HBA are reported in Fig. 2 in a similar study to that reported in the previous section. The experimental conditions used for the electrolyses are similar regarding the electrolysis cell, current density and concentrations of the organic compounds. Concerning the electrolyses of 2,3-HBA as a single starting organic compound (circles), results are similar to those obtained for BA, as an exponential decay is observed even though the consumption of 2,3-HBA is much faster than that of BA (compare the electrolysis time scales of Fig. 1 and Fig. 2). Based on this evidence, identical conclusions can be drawn concerning the establishment of a steady concentration of HO radicals at the anode surface along the electrolysis of 2,3-HBA. The solid line fitted to experimental data in Fig. 2 was simulated using eq. A.15 in the same manner as it is done for BA.

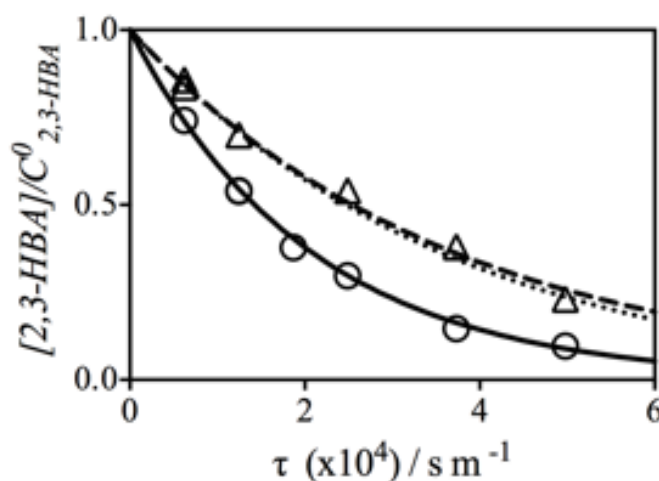


Figure 2. Concentration decrease of 2,3-HBA along time, $C^0_{2,3-HBA} = 0.50$ mM during a galvanostatic electrolysis at 1250 A m^{-2} in the absence (O) and in the presence (Δ) of 4-HBA. Experimental data are plotted together with simulated curves considering eq. A.15 using (solid line), eq. B.11 (dotted line) and eq. B.9 (dashed line) and using the following kinetic parameters: $(2 k_{O_2} + CS) / k_{2,3-HBA,HO} = 419 \text{ mol m}^{-3}$,

$$\overline{n_{4-HBA,P_{4-HBA}} k_{4-HBA,P_{4-HBA}}} / k_{2,3-HBA,HO} = 1906 \text{ mol m}^{-3}, k_{C(4-HBA,P)} = 5.0 \times 10^{-6} \text{ m s}^{-1}, k_{2,3-HBA,e} = 21 \times 10^{-6} \text{ m s}^{-1}.$$

Results from the electrolysis of 2,3-HBA (displayed as triangles) show that its consumption in the presence of 4-HBA slows down appreciably. The concentration decrease follow an exponential decay with an apparent rate constant, k_{app} , lower than the k_{app}^0 of 2,3-HBA. Experimental data were simulated using eq. B.9 and eq. B.11. The curves adjusted using both equations fit quite well to experimental data, showing that the protective effect of 4-HBA does not decrease noticeably in the experimental time range. It should be mentioned that the value of the rate constant used to describe the decrease of [4-HBA] and of [P_{4-HBA}] along time ($k_{C(4-HBA,P)} = 5.0 \times 10^{-6} \text{ m s}^{-1}$) is identical to that used in the previous section.

These results in conjunction with the reported in section 3.1 for BA demonstrate that k_{app} is susceptible to the occurrence of secondary reactions involving HO radicals. Furthermore, depending of the time span of the experiments, k_{app} can be rather constant or may decrease along time.

In order to validate eq. B.8, eq. B.9, eq. B.10 and eq. B.11 used to fit experimental data in Fig. 1 and Fig. 2, additional experiments were carried out regarding the consumption of 2,3-HBA in the presence of different concentrations of 4-HBA k_{app} should decrease with regard to k_{app}^0 with the increasing concentration of 4-HBA. Eq. B.12 predicts a linear relation between the reciprocal of the variation of the apparent rate constant ($\Delta k_{app} = k_{app}^0 - k_{app}$) and the reciprocal of the total concentration C_{4-HBA}^0 . Indeed, experimental data obtained from 0.50 mM 2,3-HBA with concentrations of 4-HBA ranging from 0.08 mM to 3.00 mM show an excellent agreement with the predicted trend. By means of a linear regression, values of intercept and slope were estimated for the straight-line represented in Fig. 3. According to eq. B.12, the intercept corresponds to $(zF/j) (2 k_{O_2} + CS) / k_{2,3-HBA,HO}$ and allow to estimate a value

of 431 mol m^{-3} for $(2 k_{O_2} + CS) / k_{2,3-HBA,HO}$, that is comparable to 419 mol m^{-3} used to simulate the experimental data in Fig. 2 concerning an initial concentration of 4-HBA of 0.50 mM . Regarding the meaning of the slope given by eq. B.12, and combining the values of the slope and intercept ($\text{intercept}^2/\text{slope}$) a value of 1992 mol m^{-3} is estimated for $\overline{n_{4-HBA,P_{4-HBA}} k_{4-HBA,P_{4-HBA}} / k_{2,3-HBA,HO}}$ that is similar to the value (1906 mol m^{-3}) used to simulate experimental results in Fig. 2.

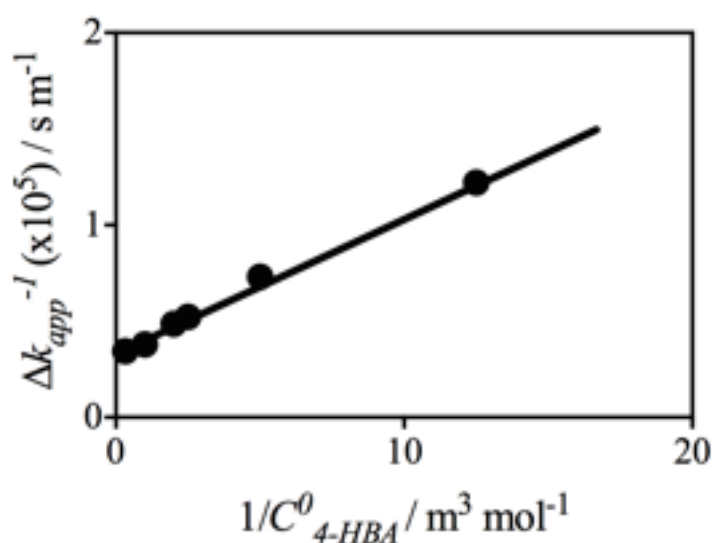


Figure 3. Representation of the reciprocal of the variation of k_{app} of $C_{2,3-HBA}^0 = 0.50 \text{ mM}$ 2,3-HBA as a function of the reciprocal of concentration of 4-HBA. Dotted line is obtained by linear regression ($1/\Delta k_{app} = (3.3 \pm 0.1) \times 10^4 + (7.2 \pm 0.2) \times 10^3 1/C_{4-HBA}^0$).

3.3. Effect of the presence of the actual reaction products

The formation of reaction products that can react with HO radicals was pointed out above as the reason for obtaining constant values of k_{app}^0 . In terms of the model used to simulate experimental data this effect is accounted by the term CS defined by eq. A.14. The increase of concentration of the reaction products along the electrolysis could therefore compensate the concentration decrease of the initial organic compound, thus keeping CS constant during an electrolysis. However considering

electrolyses with different concentrations of the starting organic compound, the value of k_{app}^0 obtained from each electrolysis should vary if the contribution of the term CS is relevant with respect to k_{O_2} (eq. A.15), given the dependence of CS on $[S]$ and $[P_{s,i}]$ (eq. A.14). The concentration decrease of BA, 2-HBA, 4-HBA and 2,3-HBA from electrolyses conducted at different initial concentrations is shown in Fig. 4. Despite

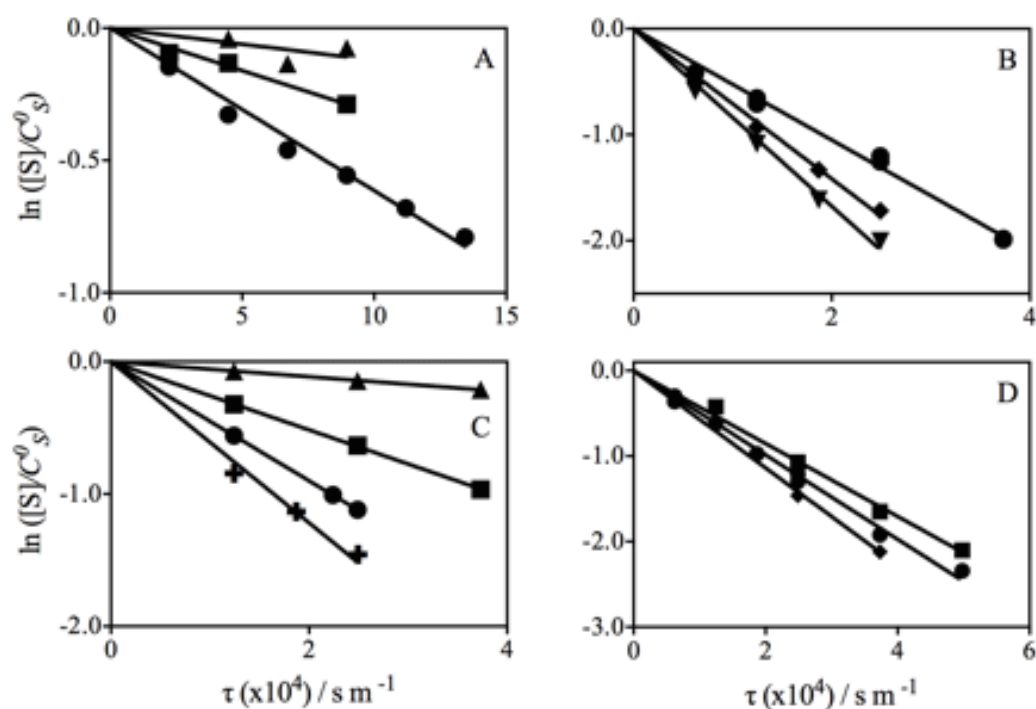


Figure 4. Concentration decrease during galvanostatic electrolyses at $1250 A m^{-2}$ of BA (A), 2-HBA (B), 4-HBA (C) and 2,3-HBA (D) at different initial concentrations, C_s^0 : 5.00 mM (▲), 1.00 mM (■), 0.50 mM (●), 0.25 mM (●), 0.10 mM (◆) and 0.05 mM (▼).

the magnitude of the initial concentrations, that was varied between 0.05 to 5.00 mM, exponential concentration decreases are observed, that are characteristic of pseudo-first order reactions. Results also indicate a pronounced dependency between the rate of consumption of each compound and its initial concentration, demonstrating that CS is comparable to k_{O_2} . The attainment of constant values of k_{app} along an electrolysis implies that CS remains constant during the experiment time span. Furthermore, the more effective concentration decreases are obtained for lower initial concentrations,

i.e. for the lower values of C_S , what is in accordance with the predicted by eq. A.13 and eq. A.15. The dependence of k_{app}^0 on concentration is more pronounced for the non-electroactive BA and 4-HBA. Indeed this fact can be easily understood, since for electroactive species only the parcel of k_{app}^0 associated to the reaction involving HO radicals, $k_{app,HO}^0$, is affected by the variation of the initial concentration, while the rate constant of the direct electron transfer reaction, $k_{S,e}$, does not depend on the species concentration.

The dependency of k_{app}^0 on the initial concentration of the species in each electrolysis is illustrated in Fig. 5. Concerning the non-electroactive species (Fig. 5A and Fig.5C) the representation is $1/k_{app}^0$ vs C_S^0 (eq. A.22), whereas for the electroactive species the corresponding representation (Fig. 5B and Fig.5D) is $1/k_{app,HO}^0$ vs C_S^0 (eq. A.24).

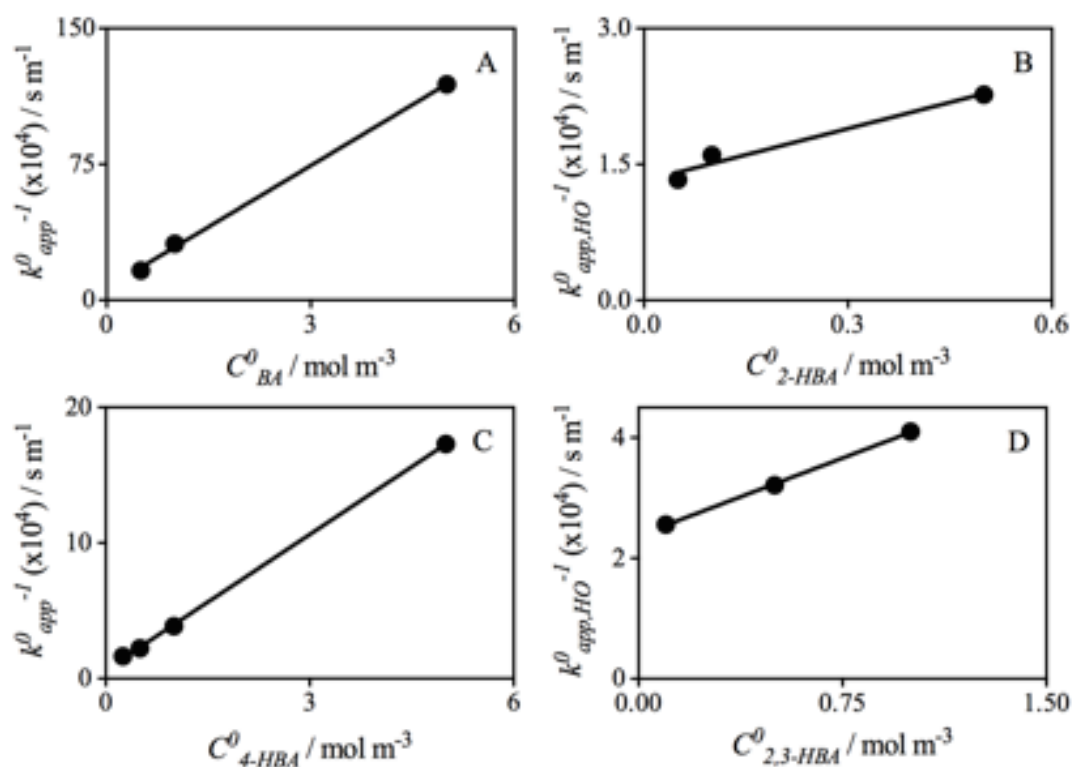


Figure 5. Representation of the reciprocal of k_{app}^0 vs the initial concentration for: BA (A), and 4-HBA (C); and of the reciprocal of $k_{app,HO}^0$ vs the initial concentration for: 2-HBA (B) and 2,3-HBA (D).

Values of $k_{app,HO}^0$ were calculated by $k_{app}^0 - k_{S,e}$ where values of $k_{S,e}$ were estimated from the intercept of k_{app}^0 vs j [19]. The obtained linear correlations are quite good for the four aromatic compounds, demonstrating that the parameters ascribed to the intercept and to the slope remain constant despite the change of the initial concentration. Considering the relations expressed by eq. A.22 and eq. A.24, from the intercept it can be estimated the value of $k_{S,HO} / k_{O_2}$. Values of $k_{S,HO} / k_{O_2}$ for BA, 2-HBA, 4-HBA and 2,3-HBA are presented in Table 1. From the slope of $1 / k_{app,HO}^0$ vs C_S^0 values of $\overline{n_{S,P} k_{S,P}} / k_{S,HO}$ ($= \overline{n_{S,P}} \overline{k_{S,P}} / k_{S,HO}$) are obtained. This amount corresponds to the product of the average stoichiometric coefficients by the average rate constants, regarding the original species S and products P , divided by the rate constant of S . An estimation of the average stoichiometric coefficients, $\overline{n_{S,P}}$, can be obtained by assuming that $\overline{k_{S,P}} / k_{S,HO} = 1$. The error of this estimation depends on the relative weight of $k_{S,HO}$ on the calculation of $\overline{k_{S,P}}$, (eq. A.19). As this average value is calculated by a weighted arithmetic mean, regarding the concentrations of each species, the correspondence between $\overline{k_{S,P}}$ and $k_{S,HO}$ can be fairly accepted for low conversion levels of S . On the other side, for high conversion levels of S , the error of this approximation should not exceed one order of magnitude. This assumption is made considering the differences between the values of $k_{S,HO} / k_{O_2}$ of the different compounds (Table 1). Besides, if the difference between $k_{S,HO}$ and $\overline{k_{S,P}}$ is significantly large, a steady k_{app}^0 will certainly not be obtained. As this was not the case for any of the analysed set of data (in Fig. 4), we can therefore accept the assumption of $\overline{k_{S,P}} / k_{S,HO} = 1$.

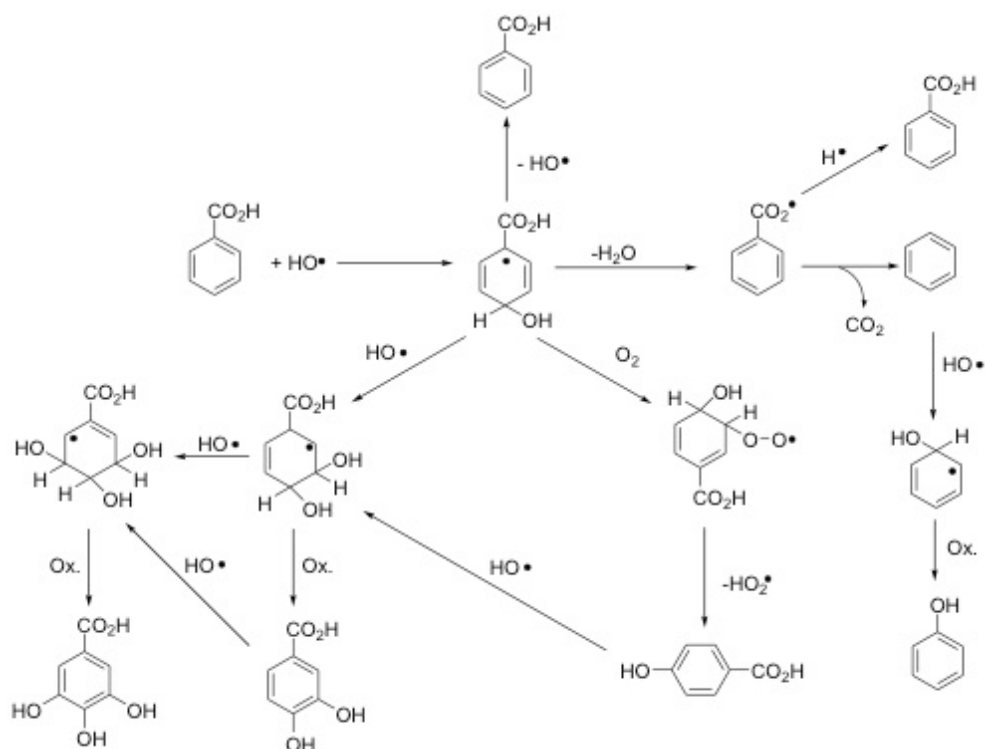
The estimated values of $\overline{n_{S,P}}$ for BA, 2-HBA, 4-HBA and 2,3-HBA are displayed in Table 1. The quite unexpected high values obtained for $\overline{n_{S,P}}$ require some reflection and careful analysis concerning a possible mechanistic interpretation of this evidence.

3.4. Mechanistic interpretation of the HO radical stoichiometric coefficients

The amazingly high values of $\overline{n_{S,P}}$, that range from 190 (from 2-HBA) to 2,900 (from BA), can only be explained considering that reaction products and intermediaries formed by reaction with HO radicals are involved in subsequent reactions that make possible to regenerate reactive species that persist in scavenging HO radicals.

Compounds with aromatic rings, such as BA or 4-HBA, are readily attacked by HO radicals giving a variety of free radical aromatic species as it is shown in scheme 1.

There are several reports describing the reaction of aromatic compounds with HO radical [15,19,21]. The addition of HO radicals to this type of compounds gives hydroxycyclohexadienyl radical intermediates that are easily oxidized to give several hydroxylated derivatives (scheme 1). The 4-HBA is one of the major products isolated from the oxidation of BA [15]. This is probably due to the stability of the corresponding hydroxycyclohexadienyl radical. Dehydration of the hydroxycyclohexadienyl radicals can also occur giving a BA radical that can be decarboxylate or can regenerate BA. As the reactivity of electrogenerated HO radicals can be quite low, as a result of the strong adsorption strength at Pt, the rate of HO radical addition to aromatic ring can be lower than that of dehydration reactions. As a result, the number of HO radicals involved in the reaction, $\overline{n_{S,P}}$, can exceed the number of radicals required for the species mineralization.



Scheme 1. Possible reactions involved in the attack of hydroxyl radicals to benzoic acid.

4. Conclusions

The rate of consumption of aromatic compounds by electrogenerated HO radicals depends strongly on the presence of other species that are potential HO radicals scavengers. The effect of the presence of 4-HBA on the apparent rate constants of BA and 2,3-HBA and the effect of the presence of 2-HBA on the apparent rate constant of BA was similar, in the sense that a substantial decrease in the rate of consumption of BA and of 2,3-HBA was noticed. The magnitude of this effect was shown to depend not only on the concentration of the radical scavenger but also on its reactivity towards HO radical, that was characterized by $\overline{n_{R,P}k_{R,P}}$, i.e. by the average value of the product between the stoichiometric coefficients and the rate constants of reactions of R and of its reaction products with HO radicals.

The products formed from the reaction between aromatic compounds and HO radicals can themselves be HO radicals scavengers and therefore compete with the reactant for

these radicals. This assumption was considered to explain the apparent disagreement between the dependency of apparent rate constants (k_{app}^0) on the concentration. While k_{app}^0 depended on the initial concentration of the species, k_{app}^0 remained constant during each electrolysis (despite the concentration decrease). By considering that the HO radical concentration is controlled by both, starting species and reaction products, an expression was deduced that allows to estimate important reactivity parameters such as $k_{S,HO} / k_{O_2}$ (ratio between the rate constant of reaction of S with HO radical and the rate constant of O_2 formation) and $\overline{n_{S,P}}$ (average stoichiometric coefficients regarding the original species S , products and intermediaries P). The high values estimated for $\overline{n_{S,P}}$, from all the analysed compounds (BA, 2-HBA, 4-HBA and 2,3-HBA), indicates that dehydration reactions can play an important role in stabilizing reaction intermediaries in conditions where the availability of HO radicals (with sufficient energy to react, as a result of their strong adsorption strength at Pt) is quite low.

Appendix A

The consumption of an organic compound, S , by galvanostatic electrolysis, with simultaneous O_2 evolution is considered in view of the following conditions and assumptions:

- The starting compound reacts with electrogenerated HO radicals and originate products that may also react with these radicals;
- The starting compound and its reaction products may be electroactive;
- The rate of all reactions (including the heterogeneous charge transfer) is slow relative to diffusion, so that concentration polarization can be neglected.

The consumption of organic compounds by galvanostatic electrolysis, with simultaneous O₂ evolution, is related to the formation of HO radical, as an intermediary species, according to the global reactions described by eq. A.1 and eq. A.2 [22,23].



The rate of formation of radicals, v_{HO} , is controlled by the current density j (A m⁻²), according to eq. A.3 [22,23].

$$v_{HO} = \frac{j}{zF} \quad (A.3)$$

where z corresponds to the stoichiometric factor and F to the Faraday constant. The reaction between HO radicals and a chemical species, S , is expressed by eq. A.4. As the products formed by this reaction may also be react with HO radicals in subsequent reactions, eq. A.5 must be considered as well:



where $P_{S,i}$ ($i = 1, 2, \dots, n$) corresponds to intermediaries or chemical species formed by direct or subsequent reactions of S with HO radicals and $k_{S,HO}$ and $k_{P_{S,i},HO}$ are the corresponding rate constants.

The rate of formation of HO radicals in steady state conditions can be defined as:

$$v_{HO} = 2v_{O_2} + n_S v_{S,HO} + \sum n_{P_{S,i}} v_{P_{S,i},HO} \quad (A.6)$$

where v_{O_2} , the rate of formation of oxygen according to eq. A.2, can be defined as follows:

$$v_{O_2} = k_{O_2} \Gamma \theta \quad (\text{A.7})$$

where $\Gamma \theta$ corresponds to the surface concentration of HO radicals at the anode surface; θ is the surface coverage degree and Γ the saturation concentration of this species (mol m^{-2}). The rate of reaction between the chemical species S and the HO radical is defined by:

$$v_{S,HO} = k_{S,HO} [S] \Gamma \theta \quad (\text{A.8})$$

Considering eq. A.3, eq. A.7 and eq. A.8, eq. A.6 can therefore be rewritten as follows:

$$\frac{j}{zF} = 2k_{O_2} \Gamma \theta + n_S k_{S,HO} [S] \Gamma \theta + \sum n_{P_{S,i}} k_{P_{S,i},HO} [P_{S,i}] \Gamma \theta \quad (\text{A.9})$$

or in an equivalent form:

$$\Gamma \theta = \frac{j}{zF} \frac{1}{2k_{O_2} + n_S k_{S,HO} [S] + \sum n_{P_{S,i}} k_{P_{S,i},HO} [P_{S,i}]} \quad (\text{A.10})$$

Combining eq. A.8 and eq. A.10 it is possible to defined the consumption rate trough eq. A.11:

$$v_{S,HO} = \frac{j}{zF} \frac{k_{S,HO}}{2k_{O_2} + n_S k_{S,HO} [S] + \sum n_{P_{S,i}} k_{P_{S,i},HO} [P_{S,i}]} [S] \quad (\text{A.11})$$

According to eq. A.11 the apparent rate constant associated to the consumption of S is described by the expression:

$$k_{app}^0 = \frac{j}{zF} \frac{k_{S,HO}}{2k_{O_2} + n_S k_{S,HO} [S] + \sum n_{P_{S,i}} k_{P_{S,i},HO} [P_{S,i}]} \quad (\text{A.12})$$

A simplified expression equivalent to eq. A.12 can be written as:

$$k_{app}^0 = \frac{j}{zF} \frac{1}{(2k_{O_2} + CS)/k_{S,HO}} \quad (A.13)$$

By defining the quantity CS as follows:

$$CS = n_S k_{S,HO} [S] + \sum n_{P_{S,i}} k_{P_{S,i},HO} [P_{S,i}] \quad (A.14)$$

For species that are electroactive eq. A.13 must incorporate an additional term concerning the consumption of the species by direct electron transfer, $k_{S,e}$ [19].

$$k_{app}^0 = \frac{j}{zF} \frac{1}{(2k_{O_2} + CS)/k_{S,HO}} + k_{S,e} \quad (A.15)$$

At each moment the sum of the concentration of the species S and the concentration of all the products $P_{S,i}$ is equal to C_S^i , according to eq. A.16.

$$C_S^i = [S] + \sum [P_{S,i}] \quad (A.16)$$

The concentration C_S^i is related to the initial concentration of S, C_S^0 , by:

$$C_S^i = C_S^0 e^{k_{C(S,P)} t} \quad (A.17)$$

where $k_{C(S,P)}$ is a rate constant that expresses the decay of concentration of the species, either S or $P_{S,i}$ that can act as HO radical scavengers.

Eq. A.18 is defined combining eq. A.14 with eq. A.16:

$$\overline{n_{S,P} k_{S,P}} = \frac{CS}{C_S^i} \quad (A.18)$$

This equation defines a weighted arithmetic mean of the product between the stoichiometric coefficients and the rate constants of reactions (considering both species S and products $P_{s,i}$), where the weigh is the concentration of each species.

In circumstances where a constant value of CS is obtained (i.e. the concentration decay follow a exponential trend), CS must not decrease significantly, i.e., $C^i_S = C^0_S$.

This situation is likely to occur for short times where the extent of mineralization or ring cleavage is low. Thus, eq. A.18 can be replaced by:

$$\overline{n_{S,P}k_{S,P}} = \frac{CS}{C^0_S} \quad (\text{A.19})$$

The apparent rate constant can therefore be rewritten as,

$$k_{app}^0 = \frac{j}{zF} \frac{1}{(2k_{O_2}/k_{S,HO} + \overline{n_{S,P}k_{S,P}}C^0_S/k_{S,HO})} \quad (\text{A.20})$$

for non-electroactive species or, as

$$k_{app}^0 = \frac{j}{zF} \frac{1}{(2k_{O_2}/k_{S,HO} + \overline{n_{S,P}k_{S,P}}C^0_S/k_{S,HO})} + k_{S,e} \quad (\text{A.21})$$

for electroactive species.

For non-electroactive species, a linear relation can be established between the reciprocal of k_{app}^0 with C^0_S , as follows:

$$\frac{1}{k_{app}^0} = \frac{zF}{j} \left(\frac{2k_{O_2}}{k_{S,HO}} + \frac{\overline{n_{S,P}k_{S,P}}}{k_{S,HO}} \right) \quad (\text{A.22})$$

For an electroactive species, it is defined:

$$k_{app,HO}^0 = k_{app}^0 - k_{S,e} \quad (\text{A.23})$$

and a similar relation to eq. A.22 can also be defined:

$$\frac{1}{k_{app,HO}^0} = \frac{zF}{j} \left(\frac{2k_{O_2}}{k_{S,HO}} + \frac{n_{S,P}k_{S,P}}{k_{S,HO}} C_S^0 \right) \quad (A.24)$$

Appendix B

The consumption of an organic compound, S , by galvanostatic electrolysis, with simultaneous O_2 evolution is considered in the presence of a second organic species, R , that compete with S to the electrogenerated HO radicals. The conditions and assumptions considered are similar to those presented in appendix A.

The reaction between HO radicals with the chemical species, R , as well as with the reaction products or intermediaries of R , $P_{R,i}$ ($i = 1, 2, \dots, n$), can be described by equations similar to eq. A.4 and eq. A.5. For these reactions the rate constants are $k_{R,HO}$ and $k_{P_{R,i},HO}$ and the corresponding stoichiometric coefficients are n_R and $n_{P_{R,i}}$.

In steady state conditions the rate of formation of HO radicals is defined by eq. B.1, that includes all the processes involving formation / consumption of HO radicals already considered in eq. A.6 as well as reactions with the species R and $P_{R,i}$:

$$v_{HO} = 2v_{O_2} + n_S v_{S,HO} + \sum n_{P_{S,i}} v_{P_{S,i},HO} + n_R v_{R,HO} + \sum n_{P_{R,i}} v_{P_{R,i},HO} \quad (B.1)$$

Therefore, the apparent rate constant for the reaction of S with electrogenerated HO radicals in the presence of R can be defined as:

$$k_{app}^0 = \frac{j}{zF} \frac{k_{S,HO}}{2k_{O_2} + n_S k_{S,HO} [S] + \sum n_{P_{S,i}} k_{P_{S,i},HO} [P_{S,i}] + n_R k_{R,HO} [R] + \sum n_{P_{R,i}} k_{P_{R,i},HO} [P_{R,i}]} \quad (B.2)$$

in a similar way as for eq. A.12.

Defining the quantity CR as:

$$CR = n_R k_{R,HO} [R] + \Sigma n_{P_{R,i}} k_{P_{R,i},HO} [P_{R,i}] \quad (B.3)$$

and C_R^i as:

$$C_R^i = [R] + \Sigma [P_{R,i}] \quad (B.4)$$

where C_R^i is related to the initial concentration of R , C_R^0 , by:

$$C_R^i = C_R^0 e^{k_{C(R,P)} t} \quad (B.5)$$

where $k_{C(R,P)}$ is the rate constant that express the concentration decay of either R or $P_{R,i}$ that can act as HO radical scavengers.

Combining eq. B.3 with eq. B.4 eq. B.6 is therefore defined as:

$$\overline{n_{R,P} k_{R,P}} = \frac{CR}{C_R^i} \quad (B.6)$$

Similarly to eq. A.18, eq. B.6 defines a weighted arithmetic mean of the product between the stoichiometric coefficients and the rate constants of reactions with HO radicals.

For short times, the extent of mineralization or ring cleavage is low and a constant CR is predicted, therefore $C_R^i = C_R^0$:

$$\overline{n_{R,P} k_{R,P}} = \frac{CR}{C_R^0} \quad (B.7)$$

The apparent rate constant for short times can thus be defined attending to eq. B.2, eq. B.3 and eq. B.7:

$$k_{app} = \frac{j}{zF} \frac{1}{\left(\frac{2k_{O_2} + CS}{k_{S,HO}} + \frac{n_{R,P} k_{R,P}}{k_{S,HO}} C_R^0 \right)} \quad (\text{B.8})$$

for non-electroactive species, or by:

$$k_{app} = \frac{j}{zF} \frac{1}{\left(\frac{2k_{O_2} + CS}{k_{S,HO}} + \frac{n_{R,P} k_{R,P}}{k_{S,HO}} C_R^0 \right)} + k_{S,e} \quad (\text{B.9})$$

for the case of electroactive species.

For long times, the apparent rate constant is defined on the basis of eq. B.2, eq. B.3

and eq. B.6:

$$k_{app} = \frac{j}{zF} \frac{1}{\left(\frac{2k_{O_2} + CS}{k_{S,HO}} + \frac{n_{R,P} k_{R,P}}{k_{S,HO}} C_R^0 e^{k_{C(R,P)} t} \right)} \quad (\text{B.10})$$

for non-electroactive species, or by:

$$k_{app} = \frac{j}{zF} \frac{1}{\left(\frac{2k_{O_2} + CS}{k_{S,HO}} + \frac{n_{R,P} k_{R,P}}{k_{S,HO}} C_R^0 e^{k_{C(R,P)} t} \right)} + k_{S,e} \quad (\text{B.11})$$

for the case of electroactive species.

The effect of the presence of the species R can therefore be evaluated from the

variation of the apparent rate constants as $\Delta k_{app} = k_{app}^0 - k_{app}$. Considering the

difference between eq. A.20 and eq. B.8 or the difference between eq. A.21 and eq.

B.9, eq. B.12 is defined for both electroactive and non-electroactive species.

$$\frac{1}{\Delta k_{app}} = \frac{zF}{j} \left(\frac{2k_{O_2} + CS}{k_{S,HO}} + \left(\frac{2k_{O_2} + CS}{k_{S,HO}} \right)^2 \frac{k_{S,HO}}{n_{R,P} k_{R,P}} \frac{1}{C_R^0} \right) \quad (\text{B.12})$$

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