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Indirect electrochemical oxidation of substituted polycyclic aromatic hydrocarbons to corresponding *para*-quinones with potassium bromide in water-chloroform medium

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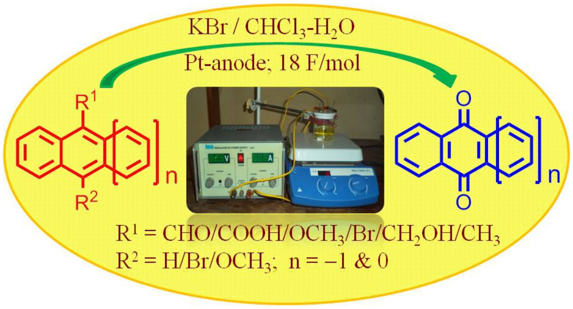
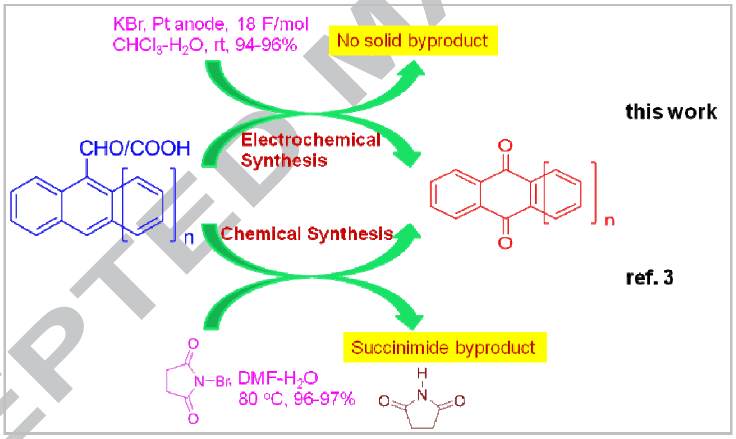


Abstract

Indirect electrochemical synthesis of quinone derivatives of a series of substituted anthracene and naphthalene by the electrolysis of aqueous solution of potassium bromide (3.0 M) using Pt anode at the constant current density (40 mA/cm^2) has been carried out. These reactions resulted in good to excellent yields of corresponding *para*-quinones as confirmed by physical and spectral data.

The synthesis of quinone derivatives has received much attention[1] because it is the starting point in the manufacture of a wide variety of industrially valuable products[2] such as dyes, pigments, DNA intercalation agents, pharmaceutically active compounds, and other newer materials. As a result, intense synthetic efforts have been devoted to the development of methods that would yield quinones.[1,2] In this context, recently we reported[3] a mild and one-pot conversion of deactivated polycyclic aromatic hydrocarbons into corresponding *para*-quinones by hypobromous acid (HOBr) generated *in situ* from the aqueous *N*-bromosuccinimide (Scheme 1). Although this method carries several advantages including metal-free, shorter reaction time and insensitive to the moisture and oxygen, there are some limitations, i.e., the reactions occurred at elevated temperature (75-80 °C) and the byproduct, succinimide, need to be removed after reaction to obtain the pure product.[3] Thus, we decided to develop a practical and environmentally friendly procedure for the preparation of quinones using HOBr.[4]

Electrochemical synthesis[5] has been realized as a promising alternative route to a conventional chemical method. Furthermore, indirect electrochemical preparations[6] (also called mediated electrochemical syntheses) in comparison with direct electrochemical methods have, in general, important advantages such as low consumption of electricity, avoiding passivation of the electrode surface, require less posterior purification, and even electrochemically inactive and/or unstable substrates can be used for the reaction.[5,6] The concepts of indirect electrochemical synthesis have frequently been used in the preparations of alkyl-,[7] benzyl-[8] and arene halides,[8,9] benzoxazoles,[10] epoxides,[11] halohydrins,[11] as well as for the degradation of hydrocarbon-[12] and cyanide[13] pollutants. Curiously, electrochemical mediated approaches have not being extended to the production of quinones particularly from polycyclic aromatic hydrocarbons substituted with either $-$CHO or $-$COOH or $-$Br or $-CH_2OH$ and so on.[5-9] This omission is probably due to the low reactivity of substituted aromatic hydrocarbons while comparing with unsubstituted analogues.[14] The interest in the substituted polycyclic aromatic hydrocarbons (SPAHS) was spurred by the fact that they are available readily in pure form, stable under different reaction conditions, and can be readily converted to the desired compounds in the later stages of multistep organic syntheses.[2,15] Herein, we describe a novel and efficient protocol for the electrochemical synthesis of 9,10-anthraquinone (**AQ**) and 1,4-naphthoquinone (**NQ**), respectively, from their mono- and disubstituted hydrocarbons by HOBr *in situ* generated by hydrolysis of bromine (Br_2) produced from aqueous potassium bromide (KBr) through electrolysis (Scheme 1). Reaction conditions such as current density, electrolyte concentration and the medium pH were optimized using 9-anthraldehyde (**1A**) as the model substrate. To the best of our knowledge, synthesis of *para*-quinones from SPAHS has not been investigated in detail.



Scheme 1. Synthetic routes to *para*-quinones

To make sure the formation of HOBr, under the experimental conditions used here, first we electrolyzed the aqueous solution of KBr in the absence of hydrocarbon substrate. Figure 1 shows the typical voltammograms obtained from aqueous solution of KBr (1.0 mM) containing potassium nitrate (KNO_3, 1.0 M) as supporting electrolyte at a scan rate of 50 mV/s. One may notice that the reversible profile with anodic and cathodic peak potentials are at 1.02 V vs. SCE and 0.83 V vs. SCE, respectively, corresponding to the two electrons transformation of bromide (Br^-) to Br_2 (eq. 1)[6] and vice versa. This electrochemically generated Br_2 can react with either water or hydroxide ions produced at cathode to form HOBr (eqs. 2 and 5).[16] It was demonstrated by UV-vis spectroscopy. As can be seen in Figure 1, the aqueous solution of KBr did not show any absorption in the spectra. Whereas the spectra measured immediately after electrolysis (< 1 min) display intense peak characteristic for Br_2 at 396 nm.[16] This band gradually decreased with solution aging and concomitantly a new peak at 266 nm emerged. Eventually the peak at 396 nm disappeared completely, whereas the peak at 266 nm attains a maximum. These combined observations indicate that the Br_2 generated by the electrolysis reacts immediately with H_2O yielding expected HOBr, which was reported to absorb at 266 nm.[16] HOBr is a weak acid (dissociation constant, pKa, is 7.54 at 25 °C)[4] and is recognized to dissociate to form H^+ and BrO^- (hypobromite ion) at ambient conditions. The formation of BrO^- is evidenced from the absorption maximum at 331 nm, cf. Figure 1.[16] Thus, oxidizing agents $HOBr/BrO^-$ can be generated readily by the hydrolysis of Br_2 produced by electrolysis of aqueous solution of KBr under the experimental conditions employed.

$2Br^{-} \xrightarrow{\text{1.02 V vs. SCE}} Br_2 + 2e^{-}$ eq. 1 (at anode)

$Br_2 + H_2O \rightleftharpoons HOBr + HBr$ eq. 2

$HOBr \rightleftharpoons BrO^{-} + H^{+}$ eq. 3

$2H_2O + 2e^{-} \longrightarrow 2OH^{-} + H_2$ eq. 4 (at cathode)

$Br_2 + OH^{-} \longrightarrow HOBr$ eq. 5

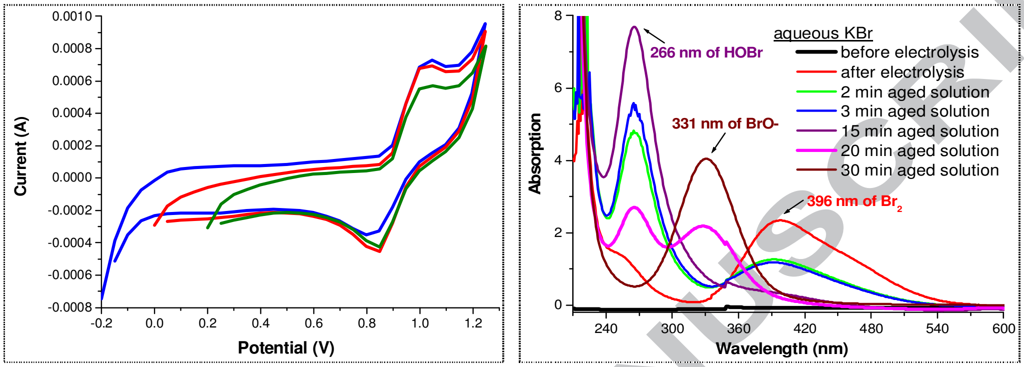


Figure 1. In left are shown the typical cyclic voltammograms of aqueous solution of KBr (1.0 mM) containing KNO_3 (1.0 M) as supporting electrolyte at a scan rate of 50 mV/s, and the absorption profiles of aqueous solution of KBr measured before and after the electrolysis are depicted in right. Notice that the absorption peak at 396 nm corresponding to Br_2 disappeared with time and new peaks appeared at 266 nm and 331 nm representing to HOBr and BrO^{-}, respectively.

The results obtained by cyclic voltammetry (Figure 1) led us to attempt the reaction between **1A** (a representative example) and $HOBr/BrO^{-}$ generated *in situ* from electrochemical oxidation of aqueous KBr. Accordingly, the preparative-scale two-phase electrolysis[17,18] was carried out in an undivided electrochemical cell supplied with two platinum sheets (Pt, $1.0 \times 1.5\ cm^2$) as an anode and a cathode. The upper phase, aqueous KBr solution (30 mL, 3.0 M), acted as a supporting electrolyte as well as Br^{-} source, whereas, the substrate (0.5 mmol) dissolved in chloroform ($CHCl_3$, 30 mL) behaved as the lower phase. The aqueous phase alone was electrolyzed galvanostatically at a current density of 20 mA/cm^2 using a DC power source.[18] In view of the fact that HOBr and the substrate (**1A**) react in a 4:1 mole ratio to yield quinones,[3] the electrolysis time was estimated to provide 8 F/mol charge consumption. The electrolysis was stopped after a charge of 8 F/mol was passed and the reaction mixture was examined by thin layer chromatography using 2% ethyl acetate in n-hexane. As we expected, the product did form, however, some unchanged **1A** persisted as well (Figure 2). After silica gel column chromatography, the product and the starting material were isolated in pure state in yields of 38% and 61%, respectively. Comparing the product's melting point, elemental analysis and ^{1}H NMR data (Figure 2) to those given in the literature, this compound was identified as 9,10-anthraquinone (**AQ**).[3,19]

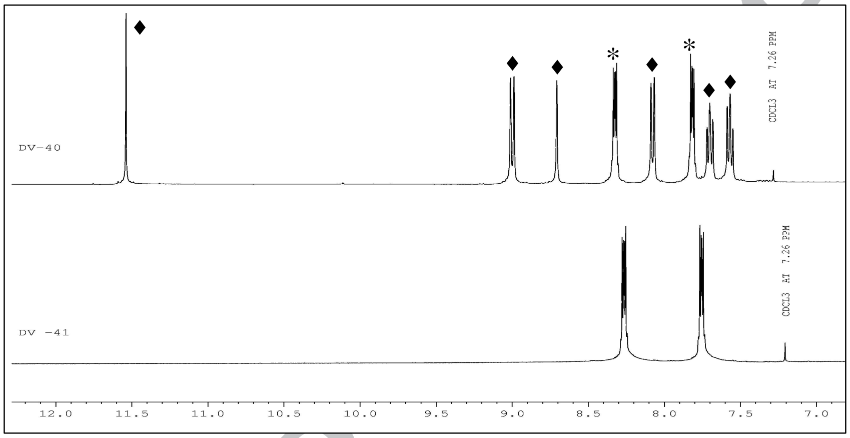


Figure 2. ^{1}H NMR (CDCl$_3$, δ = 7.26 ppm) spectra of **1A** recorded after charge of 8 F/mol (top) and 18 F/mol (bottom) were passed. Notice that more than 60% of unchanged starting material remained when the electrolysis was stopped after passing the theoretical quantity (8 F/mol) of charge. Signals arose from the starting compound and the product were indicated in symbols ♦ and *, respectively in the top figure.

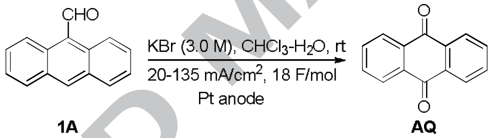
As the isolated yield of **AQ** was unsatisfactory (38%), we increased the quantity of charge more than theoretical amount, i.e. 8 F/mol. The amount of unchanged substrate (**1A**) in the reaction mixture decreased to trace amounts by prolongation of the electrolysis time (Figure 2). Thus, the consumption of 18 F/mol charge gave the product in 94 % yield (isolated). Further prolongation of the electrolysis time yielded several new side products, which could not be isolated and identified. Hence, 18 F/mol was chosen as optimum value of charge to be passed in the preparative work. In aqueous solutions oxygen evolution (1.23 V vs. SCE) is closer to the Br_2 evolution potential (1.02 V vs. SCE, cf. Figure 1).[5] In addition, some Br_2

may have escaped from the electrochemical cell into the air without being consumed. So the conversion efficiency was found to be below 40% when the electrolysis was stopped after just passing the theoretical quantity of charge.

Effect of current density on electrochemical oxidation of 1A

In order to shorten the electrolysis time, the oxidation reaction of **1A** was conducted with increased current densities from 20 mA/cm^2 to 135 mA/cm^2. Results were summarized in Table 1. While compared to lower current densities, the rate of oxidation of **1A** is maximal in increased current densities. Nevertheless, at very high current densities the product yield got decreased due to the formation of unknown side products.[5] So 40 mA/cm^2 was chosen as an optimum current density for the oxidation of SPAHS presented.

Table 1. Study on the effect of current density on the oxidation of **1A** to **AQ**.



entry	[a] current density (mA/cm^2)	time (min)	[b] product yield (%)	[c] elemental analysis (found for $C_{14}H_8O_2$, %)
1	20	468	95	C, 80.75; H, 3.87
2	25	351	94	C, 80.74; H, 3.87
3	40	234	96	C, 80.75; H, 3.86
4	65	141	89	C, 80.74; H, 3.87
5	100	94	92	C, 80.76; H, 3.87
6	135	70	85	C, 80.75; H, 3.87

All reactions were performed at identical experimental conditions except that the current density was varied from 20-135 mA/cm^2. [a] Aplab power supply was used as a direct current source for the electrolysis. [b] Yield was determined from the product isolated by recrystallization using n-hexane-ethyl acetate mixture. [c] Analytical calculated for $C_{14}H_8O_2$: C, 80.76%; H, 3.87%.

Effect of electrolyte concentration on electrochemical oxidation of 1A

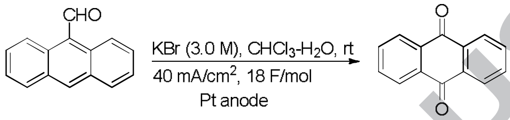
The rate of oxidation of Br^- has been known to depend on the electrolyte concentration.[5,6] Thus, we studied the oxidation reaction of **1A** in various concentrations of KBr at constant current density (40 mA/cm^2). In the presence of 0.5 M, 1.0 M, 1.5 M, 2.0 M, 2.5 M, 3.0 M, 3.5 M and 4.0 M KBr, yields of **AQ** obtained after passing 18 F/mol charge were about 15%, 40%, 55%, 73%, 78%, 93%, 96%, and 95%, respectively. The increasing yield of **AQ** with the amount of KBr indicates that the Br^- ions play an important role in the reaction through controlling the conductivity of the medium.[5] Although yields of the product (**AQ**) at higher concentrations of KBr were found to be slightly high, an electrolyte concentration of 3.0 M was selected as the operating concentration owing to vigorous evolution of Br_2/HBr as well as the known toxic effects of the Br^- excess to humans and the environment.[20] It is worthy to mention that the electrochemical experiments conducted utilizing sodium bromide as the electrolyte gave completely the same results as those performed using KBr.

Effect of pH on electrochemical oxidation of 1A

As mentioned already, HOBr is the major oxidant produced in the hydrolysis of Br_2 formed by oxidation of aqueous KBr (Figure 1). Nevertheless, HOBr is a weak acid (pKa, is 7.54 at 25 °C) and is known to dissociate into H^+ and BrO^- in the solution.[16] The concentrations of HOBr and BrO^- depend on the pH of the medium. For example, when the medium pH value is between 6.5-8 both HOBr and BrO^- can be found in water, whereas when pH is higher than the pKa, BrO^- whose nucleophilicity is greater than that of the HOBr accounted for larger proportion in the medium. Thus, the effect of different pH on the oxidation of **1A** to **AQ** was studied and the results were summarized in Table 2.

To examine the effect of pH on the oxidation reaction of **1A**, the reaction mixture was adjusted to the desired pH for each experiment using solutions of either aqueous sulphuric acid or aqueous sodium hydroxide. As shown in Table 2, the rate of oxidation of **1A** to **AQ** at basic pH was found to be a greater extent while compared to acidic solutions. In other words the reaction rate decreased gradually with the decreasing of pH from neutral to highly acidic range, whereas the addition of base to the reaction mixture led to noticeable improvements in the yield of **AQ** (Table 2). We concluded from the UV-vis measurements that in highly acidic environment the hydrolysis of Br_2 is strongly inhibited. As a result the yields of the **AQ** were found to be minimum at moderate acidic pH and practically no oxidation could be achieved in very high acidic mediums (pH ≤ 2). Therefore, pH 9 was taken an optimum value for this process as product decomposition was detected at more alkaline media.

Table 2. Study on the effect of pH on the oxidation of **1A** to **AQ**.



1A **AQ**

entry	[a] medium pH	[b] product yield (%)	[c] elemental analysis (found for $C_{14}H_8O_2$, %)
1	2	<5	C, 80.74; H, 3.88
2	4	20	C, 80.77; H, 3.86
3	6	38	C, 80.76; H, 3.87
4	8	76	C, 80.75; H, 3.88
5	10	91	C, 80.76; H, 3.86
6	12	92	C, 80.77; H, 3.88

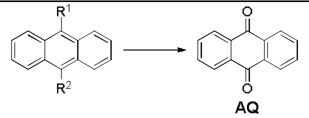
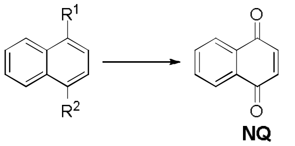
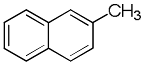
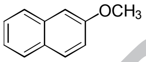
All reactions were performed at identical experimental conditions except that the medium pH was varied from 2 to 12. [a] The desired pH for each experiment was adjusted by using solutions of either aqueous sulphuric acid or aqueous sodium hydroxide. [b] Yield was determined from the product isolated by recrystallization using n-hexane-ethyl acetate mixture. [c] Analytical calculated for $C_{14}H_8O_2$: C, 80.76%; H, 3.87%.

Overall, the optimized conditions for a perfect electrochemical oxidation of **1A** to **AQ**, a representative example, are as follows. To a solution of **1A** (0.5 mmol) in 30 ml of $CHCl_3$ in an undivided cell was added aqueous solution of KBr (3.0 M, 30 ml). With the resultant two-phase solution,[17,18] the aqueous phase alone was electrolyzed galvanostatically at a constant current density of 40 mA/cm^2 until the 18 F/mol charge was passed, cf. Supporting information (SI). The temperature of the electrochemical cell contents was maintained at

25±2 °C throughout the electrolysis. After completion of the electrolysis, the lower organic phase was separated and purified.[18]

Having established the optimum conditions for the electrochemical oxidation reaction, the methodology was extended to a series of other SPAHS whose structures are shown in Table 3. Without any surprise various mono- and disubstituted derivatives of anthracene (**2A**-**8A**) and naphthalene (**9N**-**13N**) underwent an electrochemical oxidation smoothly under the optimized conditions yielding the expected **AQ** and **NQ**, respectively, in good to excellent yields. In contrast to the 1-naphthyl derivatives (**9N**-**13N**), the 2-methylnaphthalene (**14N**) and 2-methoxynaphthalene (**15N**) were prone to undergo complete oxidation under the condition studied. They yielded mixture of products after prolonged electrolysis. Therefore, the electrochemical method for the oxidation of 9- and 9,10-disubstituted anthracenes and α-substituted naphthalenes to corresponding *para*-quinones were developed using two-phase electrolysis (SI).[18] We feel that the present finding may have several advantages including low cost of production, ease of operation, simple work-up procedure and no waste handling problems when compared to classical chemical syntheses.[1-4]

Table 3. The electrochemical synthesis of **AQ** and **NQ** from various SPAHS in a water-$CHCl_3$ medium.

s. no.	[a] substrate	product	[b, c] yield (%)	[c] melting point (°C)	[c, d] elemental analysis (found for **AQ** & **NQ, %**)
					
1	**1A**, R^1 = CHO; R^2 = H	**AQ**	94	284-286	C, 80.75; H, 3.87
2	**2A**, R^1 = COOH; R^2 = H	**AQ**	91	284-286	C, 80.76; H, 3.86
3	**3A**, R^1 = OCH_3; R^2 = H	**AQ**	96	283-286	C, 80.76; H, 3.87
4	**4A**, R^1 = Br; R^2 = H	**AQ**	96	283-286	C, 80.75; H, 3.86
5	**5A**, R^1 = CH_2OH; R^2 = H	**AQ**	84	283-286	C, 80.76; H, 3.86
6	**6A**, R^1 = CH_3; R^2 = H	**AQ**	92	284-287	C, 80.76; H, 3.87
7	**7A**, R^1 = CHO; R^2 = Br	**AQ**	95	285-286	C, 80.75; H, 3.87
8	**8A**, R^1 = CHO; R^2 = OCH_3	**AQ**	94	284-286	C, 80.76; H, 3.87
					
9	**9N**, R^1 = CHO; R^2 = H	**NQ**	87	123-126	C, 75.93; H, 3.83
10	**10N**, R^1 = COOH; R^2 = H	**NQ**	92	124-126	C, 75.94; H, 3.81
11	**11N**, R^1 = Br; R^2 = H	**NQ**	74	124-126	C, 75.93; H, 3.83
12	**12N**, R^1 = CH_3; R^2 = H	**NQ**	66	125-126	C, 75.94; H, 3.82
13	**13N**, R^1 = Br; R^2 = OH	**NQ**	93	125-126	C, 75.94; H, 3.82
14	 **14N**	multiple products	61	–	–
15	 **15N**	multiple products	87	–	–

[a] All reactions were performed at constant current density (40 mA/cm^2) using aqueous KBr (3.0 M, pH = 9) as a supporting electrolyte and Br^- source. [b] Yields were determined from products isolated by either recrystallization or column chromatography. [c] Purity of compounds was established by elemental analysis and melting point determinations. [d] Analytical calculated for **AQ** ($C_{14}H_8O_2$): C, 80.76%; H, 3.87% and for **NQ** ($C_{10}H_6O_2$): C, 75.94%; H, 3.82%.

A plausible reaction mechanism for the oxidation of SPAHS into *para*-quinones has been reported by us recently.[3] The reaction starts by the electrochemical oxidation of Br^- ions at the anode yielding molecular Br_2 in the aqueous form of HOBr/BrO^- and HBr (eqs. 2 and 5 and Figure 3). The initial nucleophilic attack to the *para*-position of aromatic unit by BrO^-

results in a corresponding phenolic intermediate, which is expected to undergo *ipso*-attack by second molecule of BrO^- followed by eliminations will yield the final product (Figure 3). The appearance of only *para*-quinone as the product, among potential two quinones (*ortho*- and *para* isomers) for naphthalene compounds may be rationalized in terms of the resonance structures of the intermediate.[21] For the *para* attacked intermediate seven resonance structures can be described, of which four maintain an aromatic ring. On the other hand for the *ortho* attacked, the intermediate has only six resonance structures and only two of these are aromatic. Of course, the effect of the electronic and the steric factors of the intermediate generated in the reaction as well contributed in the stabilizations of the 1,4-naphthoquinone over 1,2-isomer.[22]

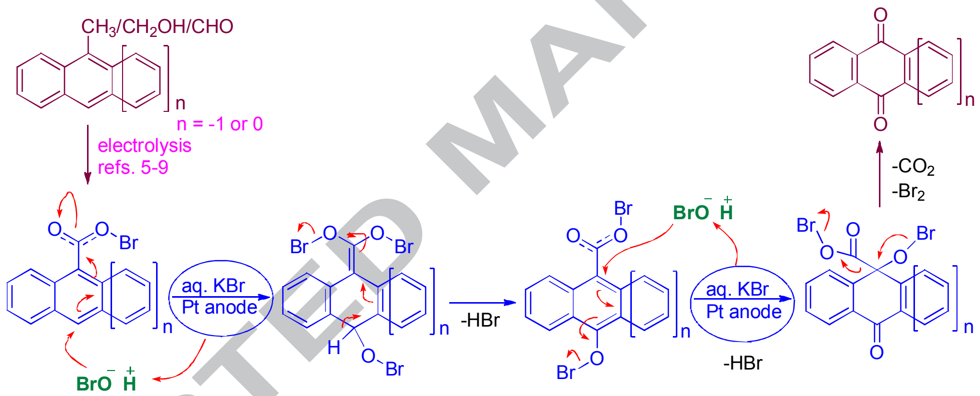


Figure 3. The proposed reaction mechanism for the electrochemical oxidation of SPAHS into the corresponding *para*-quinones.

In summary, the electrochemical method involving the oxidation of SPAHS into the corresponding *para*-quinone by two-phase electrolysis constitutes a novel and efficient alternative method over classical chemical methodologies. The yields obtained are comparable with those published for the oxidation of hydrocarbons using different oxidizing agents.[4,21]

Acknowledgements

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Supplementary data

Supplementary data (a photograph of typical electrochemical apparatus and general aspects) associated with this article can be found, in the online version, at http://dx.doi.org/00.0000/j.tetlet.0000.00.0000.

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(17) Two-phase electrolysis is one where the electrolyte and the substrate are present in different phases. When electrolysis occurs, electrolytically generated species travels from aqueous phase to organic phase and attacks the substrate; See: Christopher, C.; Lawrence, S.; John Bosco, A.; Xavier, N.; Raja, S. *Catal. Sci. Technol.* **2012**, *2*, 824–827.

(18) **Cyclic voltammetry of the aqueous solution of KBr**: Cyclic voltammograms were obtained in a Pyrex electrochemical cell containing a standard three-electrode setup (i.e., a 1 cm^2 platinum working electrode, a platinum counter electrode, and a potassium chloride saturated calomel reference electrode) connected to a potentiostat. Before analysis, the working electrode was polished with a emery paper and then rinsed with water followed by acetone and subsequently dried with air. KNO_3 was used as the supporting electrolyte. Potentials were measured at a scan rate of 50 mV/s. The potential range investigated was chosen such as to avoid the hydrogen or oxygen evolution in the aqueous electrolytic solution. Aqueous solution contained the KBr at 1.0 mM and the supporting electrolyte was KNO_3 (1.0 M). Three electrodes were placed and the potential was swept to obtain a voltammograms.

General procedure for electrochemical oxidation: To an undivided electrochemical cell the respective substrate (0.5 mmol) and $CHCl_3$ (30 mL) was added. Thirty millilitre of aqueous solution of KBr (3.0 M) was then added over the above solution. The electrolytic cell was equipped with a magnetic stirrer in order to keep the $CHCl_3$ solution well mixed. Two Pt electrodes (1.0×1.5 cm^2) were placed vertically having an inter-electrode gap of 4 cm in the aqueous phase without touching the organic phase, but very close to the interphase of the two-phases (SI). All electrolyses were performed at a constant current density (40 mA/cm^2) at room temperature. The electrolysis was stopped after passage of a charge of 18 F/mol. Subsequently, the organic layer was first collected and then the aqueous solution was extracted with two portions of dichloromethane (2 × 15 mL). The combined extracts were washed with a solution of $NaHSO_3$ (10%, 20 mL) to remove residual amounts of Br_2, then with saturated $NaHCO_3$ (10 mL), brine (10 mL) and H_2O (30 mL). After dried over anhydrous $MgSO_4$, the solvent was removed by rotary evaporation under reduced pressure and the residue was subjected to either recrystallization using n-hexane-ethyl acetate mixture (90:10, v/v) or column chromatographed over SiO_2. Yields and physical data are given in Tables 1-3.

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Indirect electrochemical oxidation of substituted polycyclic aromatic hydrocarbons to corresponding *para*-quinones with potassium bromide in water-chloroform medium

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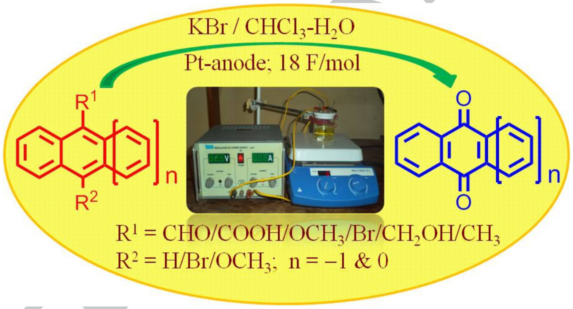

Abstract

Indirect electrochemical synthesis of quinone derivatives of a series of substituted anthracene and naphthalene by the electrolysis of aqueous solution of potassium bromide (3.0 M) using Pt anode at the constant current density (40 mA/cm^2) has been carried out. These reactions resulted in good to excellent yields of corresponding *para*-quinones as confirmed by physical and spectral data.