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Letter

Convergent Paired Electrochemical Synthesis of Azoxy and Azo Compounds: An Insight into the Reaction Mechanism

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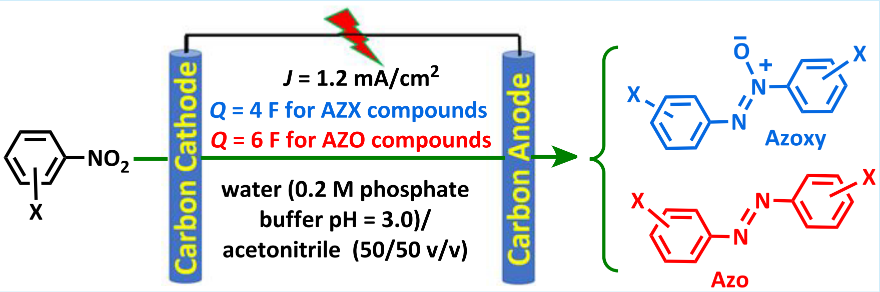

ABSTRACT: A convergent paired electrochemical method was developed for the synthesis of azoxy and azo compounds starting from the corresponding nitroarenes. We propose a unique mechanism for electrosynthesis of azoxy and azo compounds. We find that both anodic and cathodic reactions are responsible for the synthesis of these compounds. The synthesis of azoxy and azo derivatives have been successfully performed in an undivided cell, using carbon rod electrodes, by constant current electrolysis at room temperature.

Several strategies for the synthesis of azoxy and azo compounds including the use of traditional oxidants/reductants, the use of heavy metals, and electrochemical methods have been reported. In the first strategy, the synthesis of the mentioned compounds is performed through oxidation of amines or reduction of nitro compounds by various oxidants or reductants, such as H_2O_2,[1−8] I_2/DABCO,[9] tertiary butyl hydroperoxide,[10] tetrabutylammonium peroxymonosulfate[11] (Supporting Information (SI), page S7), and sodium borohydride.[12−14] Although these methods are efficient, there are some important drawbacks including the use of aromatic amines as starting toxic materials,[15] costly terms, and toxic and expensive reagents and solvents. The second strategy is the reduction of nitro compounds using heavy metals. Accordingly, various methods have been reported using samarium metal,[16] thallium metal,[17] zinc/NH_4Cl,[18] copper(I) salts,[19] palladium nanoclusters,[20] Ni-TiO_2,[21] gold nanoparticles,[22] Rh nanocrystals,[23] iridium and rhodium,[24] Ni/graphene nanocomposites,[25] Ni@C-CeO_2,[26] Au@zirconium-phosphonate nanoparticles,[27] Fe and N codoped mesoporous carbon,[28] and photoreduction.[29] These methods are valuable, and the problem of using aromatic amines has been solved. However, these methods still have disadvantages such as heavy metal pollution, toxic and expensive reagents, tedious preparation of starting materials/workup, and safety problems. In the third strategy, the synthesis of azoxy and azo compounds is performed by electrochemical methods.[30,31] In these papers, the strategy for the synthesis of azoxy compounds involves reduction of nitro compounds at the cathode surface. However, the above-mentioned methods have some disadvantages such as tedious procedures, toxic/expensive solvents and reagents, and the use of unconventional electrodes. A most important point that is not addressed in these papers is the role of the anodic reaction in the formation of azoxy compounds. Contrary to published data, we have found that both anodic and cathodic reactions are involved in the formation of azoxy compounds (convergent paired electrochemical synthesis). Some useful data on paired electrochemical processes are reported in the literature.[32] In this strategy, the overall energy consumption is 50% less than that for conventional methods.[33]

Cyclic voltammograms (CVs) of the studied halonitrobenzenes are shown in Figure 1. CVs of *p*-bromonitrobenzene (**1a**) have been recorded in two potential ranges (Figure 1 part I).

When the potential was scanned from −0.2 V to +0.4 V vs Ag/AgCl, **1a** does not show any oxidation or reduction peak (curve a). But, upon scanning the electrode potential from −0.2 V to −0.72 V (curve b), the voltammograms consist of an irreversible cathodic peak (C_0) which corresponds to a four-

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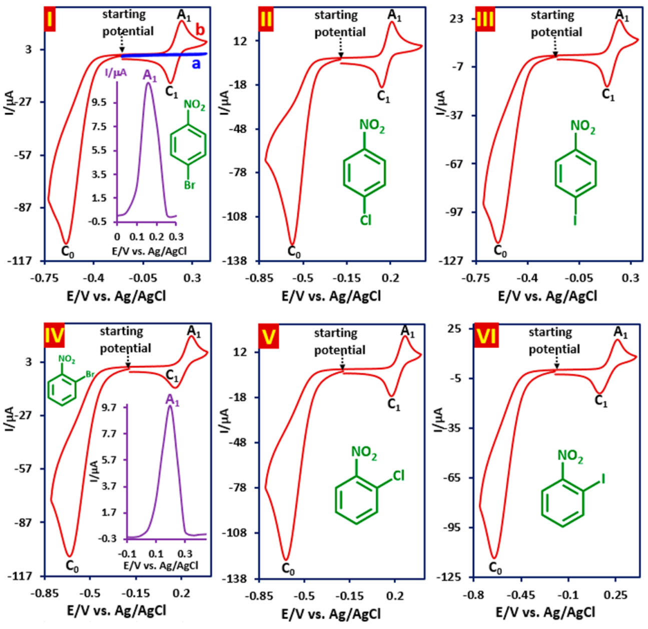
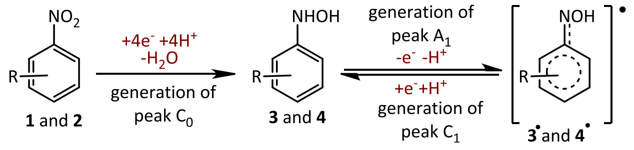


Figure 1. CVs of 1.0 mM of halonitrobenzenes at GC electrode, in aqueous solution containing phosphate buffer (c = 0.2 M, pH = 3.0)/acetonitrile (50/50 v/v). Scan rate: 100 mV/s at room temperature. Inset I, IV): Differential pulse voltammograms of *N*-(4-bromophenyl)hydroxylamine and *N*-(2-bromophenyl)hydroxylamine obtained from **1a** and *o*-bromonitrobenzene (**2a**) under the same conditions. For DPV: step potential, 50 mV; modulation amplitude, 25 mV; modulation time, 0.05 s; interval time, 0.5 s.

electron reduction of the nitro group to hydroxylamine group and a reversible redox couple corresponding to the redox activity of the phenylhydroxylamine/phenylhydroxylamine radical (**3**/**3**$^\bullet$ and **4**/**4**$^\bullet$) (Scheme 1).

Scheme 1. Reduction/Oxidation Pathway of Simple Nitro Aromatic Compounds



The pathway leading to the oxidation of cathodically generated phenylhydroxylamine (A_1/C_1) is given in Scheme 1. It should be noted that the single-electron transfer oxidation of the cathodically generated *N*-(4-bromophenyl)hydroxylamine (**3a**) has been examined using the half-peak width ($W_{1/2} = 3.52RT/nF$) of the differential pulse voltammogram of this compound (Figure 1, part I, inset).[34]

The effect of potential scan rate on CVs of **3a** has been studied, to obtain more data on the mechanism of formation of azoxy compounds (SI, page S13). The study shows that the peak current ratio (I_{pC1}/I_{pA1}) is scan rate dependent and becomes larger at faster scan rates. This finding confirms the presence of a following chemical reaction after the electron transfer step.

The effect of **1a** concentration on the voltammetric behavior of this compound is also studied (SI, page S13). It shows that I_{pC1}/I_{pA1} is concentration-dependent and becomes smaller with increasing **1a** concentration. This suggests that under the conditions that we have performed these experiments, a dimerization reaction occurs between two phenylhydroxylamine radicals (**3**$^\bullet$).[34,35]

Controlled potential coulometry (CPC) of **1a** and **2a** (*o*-bromonitrobenzene) was carried out followed by voltammetric analysis of the electrolyzed solutions (Figure 2) to identify the products and to determine the number of electrons transferred.

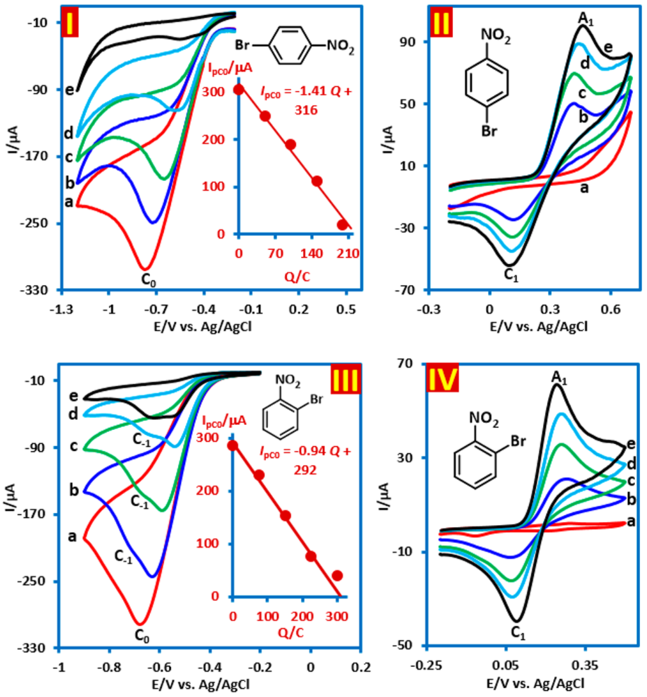
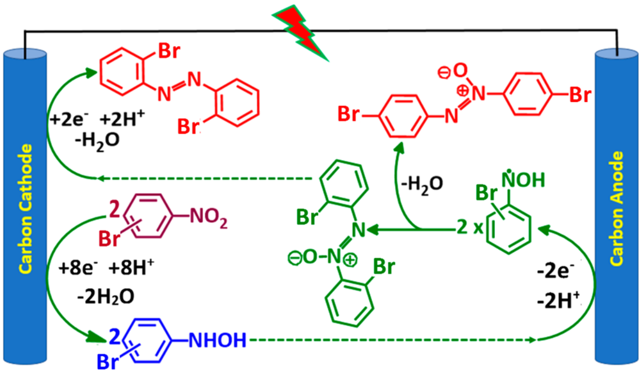


Figure 2. Part I: CVs of 0.5 mmol **1a** during CPC in an undivided cell at −1.10 V versus Ag/AgCl. Inset: variation of I_{pC0} versus consumed charge. Part II: CVs of **1a** during CPC after scanning the potential from −0.20 to +0.70 V. Voltammograms are taken after consumption of (a) 0, (b) 50, (c) 100, (d) 150, and (e) 200 C. Parts III and IV are CVs of **2a** during CPC under similar conditions with **1a** at −0.90 V after consumption of (a) 0, (b) 75, (c) 150, (d) 225, and (e) 300 C. Other conditions are similar to those in Figure 1.

Parts I and III show the effect of charge passed on the cathodic peak C_0 of **1a** and **2a**, respectively. As can be seen, I_{pC0} of **1a** gradually decreases with the progress of coulometry and disappears with the consumption of 4e$^-$ per molecule of **1a** (Figure 2, part I, inset). This number of electrons confirms the reduction of the nitro group to hydroxylamine. However, under the same conditions, the number of transferred electrons for the reduction of **2a** was calculated to be 6e$^-$ (Figure 2, part III, inset). In addition, during the electrolysis of **2a**, a new cathodic peak (C_{-1}) appears. These results show that the presence of substituent groups at different positions causes the molecule to have different electrochemical behaviors. The reason for the consumption of 6 electrons in the reduction of **2a** is stated later. Furthermore, parts II and IV of this figure show the formation and increase of the anodic and cathodic peaks A_1 and C_1 with the progress of coulometry.

The synthesis of desired products was carried out by constant-current electrolysis of nitroarenes. The suggested mechanism for the synthesis of azoxy compounds (**5**) is shown in Scheme 2. As can be seen, the cathodically generated *N*-(4-halophenyl)hydroxylamine (**3**) is oxidized at the anode to produce *N*-(4-halophenyl)hydroxylamine radical (**3**$^\bullet$). The radical coupling reaction of **3**$^\bullet$ afforded the corresponding

Scheme 2. Electrochemical Reaction Mechanism for the Synthesis of Azoxy and Azo Compounds



azoxy compound. It should be noted that, in addition to **3**, the oxidation of water at the anode causes the balance of electrons.

The reaction mechanism for the synthesis of azo compounds (**6**) is similar to that of azoxy compounds, except that the azoxy compound in the next step is reduced at the cathode and converted to the azo compound by removing a water molecule (Scheme 2). According to the Scheme 2, two molecules of *ortho*-halonitrobenzene and 10 electrons are needed to synthesize each molecule of the azo compound. Therefore, in this case, theoretically 5 electrons are consumed per *ortho*-halonitrobenzene molecule. However, in the experiments we performed in an undivided cell, due to the occurrence of phenomena such as the back reaction, the number of electrons was 6 for each *ortho*-halonitrobenzene molecule. The reduction of the *ortho*-azoxy compounds may be related to the higher solubility of these compounds compared to *para*-azoxy compounds (SI, pages S16 and S18). In addition, the observed cathodic peak C_{-1} in Figure 2, part III, is due to the reduction of the *ortho*-azoxy compound to the *ortho*-azo compound.

In order to prove the proposed mechanism, the synthesis of azoxy (or azo) compounds was also examined under exactly the same conditions in a divided cell (Figure 3). The results clearly show that no trace of the formation of the azoxy (or azo) compound was observed when a divided cell is used. In other words, the participation of the anodic process in product formation is essential.

To improve the synthetic efficiency, the synthesis of azoxy and azo compounds was also studied under constant current conditions. The effect of current density on the yield of **5a** was initially investigated (SI, page S14). These experiments were performed under the following conditions: charge consumed, 4.0 F; **1a** amount, 1.0 mmol; solvent, water (0.2 M phosphate buffer, pH = 3.0)/acetonitrile (50/50 v/v) mixture. The results show that the optimum value for the current density is 1.2 mA/cm^2 (I_{app} = 40 mA). In this current density, the yield of 79% was obtained for the synthesis of **5a**. Insufficient applied potentials for the formation of *N*-(4-bromophenyl) hydroxylamine at low current densities can be the reason for the low yield under these conditions. On the other hand, the over-reduction of **1a** at the cathode, overoxidation of *N*-(4-bromophenyl)hydroxylamine at the anode, and reduction and/or oxidation of **5a** (or solvent) are the main factors in decreasing the product yield at higher current densities.

The effect of charge consumed on the yield of **5a** was also investigated (SI, page S14). These experiments were performed under an optimum current density of 1.2 mA/cm^2. The results show that the optimum value for the charge consumed is 4.0 F which is the theoretical amount of electricity necessary for the reduction of 1.0 mmol of **1a** (Scheme 2). It seems that the reduction and/or oxidation of **5a** are the main factors in decreasing the product yield at higher charge consumed. The effect of solution pH (in the range 2−6) on the yield of **5a** under optimum conditions was also studied. Our results show that the highest yield and purity of products were obtained at pH 3.0. Similar optimizations were also performed for the synthesis of **6a**. These experiments were performed on **2a** and yielded similar results to those obtained for **5a**. The only significant difference was in the amount of electricity consumed. In this case, the optimal amount of electricity needed for the synthesis of **6a** was 6.0 F (slightly more than the theoretical value of 5.0 F). Under these conditions, the yield of 64% was obtained for the synthesis of **6a** (SI, page S9).

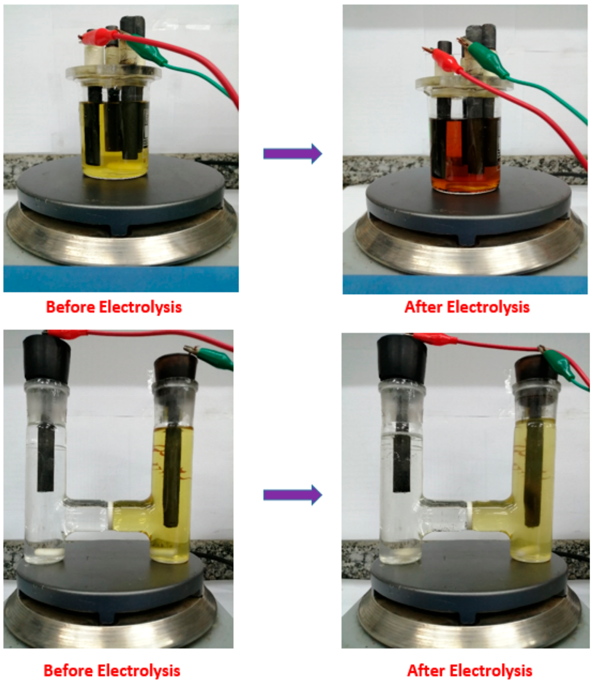


Figure 3. Constant current electrolysis of **2a** (0.5 mmol) in undivided (above) and divided (below) cells in acetonitrile/water (containing 0.2 M phosphate buffer, pH = 3.0) mixture (50/50 v/v), at room temperature. J_{app} = 1.2 mA/cm^2 (I_{app} = 40 mA).

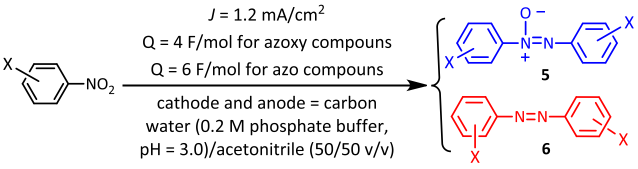
The effect of anode and cathode materials was also studied on the yield of **5a**. The results of this series of experiments are shown in Table 1. As can be seen, the maximum yield of 79% was obtained, when carbon is used for both the anode and cathode.

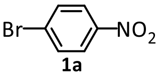
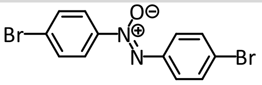
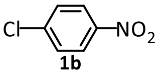
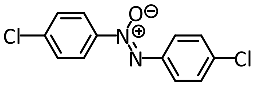
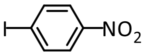
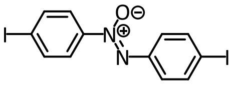
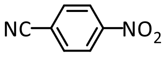
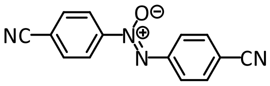
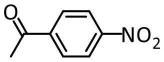
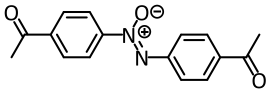
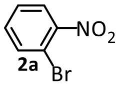
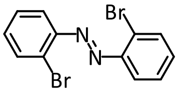
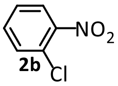
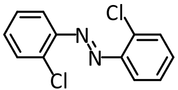
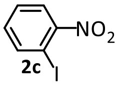
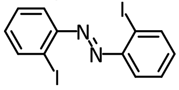
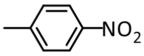
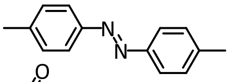
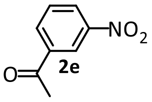
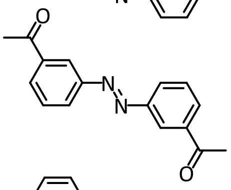
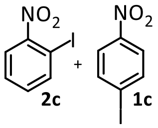
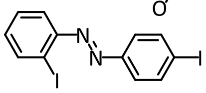
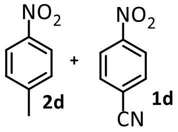
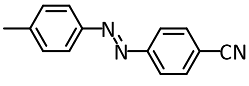
Table 1. Dependence of 5a Yield on Electrode Material

entry	cathode	anode	yield [%]
1	Carbon	Carbon	79
2	Carbon	Stainless Steel	31
3	Carbon	Cu	no reaction
4	Stainless Steel	Carbon	62
5	Zn	Carbon	38
6	Fe	Carbon	57
7	Cu	Carbon	50

The products and the yields of **5** and **6** compounds are summarized in Table 2. These data show that we were able to develop an efficient method to synthesize azoxy and azo derivatives in a one-pot reaction with a 50−86% overall yield.

Table 2. Scope of the Azoxy and Azo Derivatives Synthesis



entry	substrate	product		yield %
1	 **1a**		**5a**	79%
2	 **1b**		**5b**	81%
3	 **1c**		**5c**	77%
4	 **1d**		**5d**	86%
5	 **1e**		**5e**	85%
6	 **2a**		**6a**	64%
7	 **2b**		**6b**	70%
8	 **2c**		**6c**	67%
9	 **2d**		**6d**	63%
10	 **2e**		**6e**	78%
11	 **2c** + **1c**		**6f**	50%
12	 **2d** + **1d**		**6g**	56%

In addition to the products shown in entries 1−3 and 6−8, entries 4, 5, 9, and 10 are examples that show the method tolerates a variety of functional groups such as Cl, Br, I, CN, CH_3CO, and CH_3. In addition, entries 11 and 12 show that the proposed method can easily produce diverse products such as **6f** and **6g** through the coupling of two different nitrobenzenes and prove that the method also tolerates the combinations of different nitroarenes. In these cases, a solution containing both nitroarenes is electrolyzed under optimal conditions. The azo formation shown in entries 9−12 is probably due to the solubility of the azoxy intermediate (as it happens for *ortho*-bromo derivatives) as well as the more intense adsorption of their dependent species (SI, page S19). It also should be noted that our efforts to synthesize azo or azoxy compounds were unsuccessful, when nitroarenes have the group COOH or CHO, which is possibly due to the participation of COOH and CHO groups in the reduction process in competition with the nitro group and/or due to participation in the oxidation process in competition with the hydroxylamine group.

This method consumes less energy than other methods due to its paired strategy and also does not require catalysts, hazardous chemicals, and challenging workups. According to these characteristics, it can be concluded that the proposed method is greener than other published methods.

In this work, we discovered for the first time that the anodic oxidation of cathodically generated phenylhydroxylamine is necessary for the synthesis of titled compounds. Accordingly, we propose a convergent paired electrochemical mechanism in which the $-NO_2$ group of nitroarenes is reduced to the hydroxylamine group at the cathode surface and the cathodically generated phenylhydroxylamine compound is oxidized at the anode surface to its free radical and dimerization of radicals yields the corresponding azoxy compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c02304.

Some explanations about the optimizations, effect of pH (Pourbaix diagram), experimental details and spectral data for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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