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Communications

Green coupling of 3,5-diamino-1*H*-1,2,4-triazole into the azo compound

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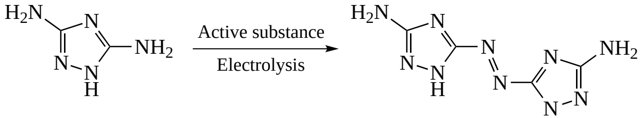
The nitrogen–nitrogen double bond between two molecules of 3,5-diamino-1*H*-1,2,4-triazole is successfully constructed using a one-step electrochemical coupling method. The oxidation occurs selectively when the electrochemical parameters are properly adjusted to provide a yield of 45.77%. Subsequently, the oxidative coupling of this substrate with electrochemically generated hydroxy nickel oxide or sodium hypochlorite is verified.



Active substance: $OH^{\bullet}$, NiOOH, NaClO

Keywords: electrochemical synthesis, conjugation reaction, active site, clean and efficient, triazoles, azo compounds, voltage control.

Triazoles were recognized as good energy-containing materials with high density, appropriate nitrogen content, high thermal performance and stability.[1,2] Traditional synthetic methods for building triazole azo derivatives are not green and convenient due to high processing temperature, requirements for strong oxidizers,[3] multistep procedures and difficulties in handling target products.[4] Dippold *et al*. employed high temperature and potassium permanganate as the oxidant to construct *N*-azo-bridged triazoles.[5] However, that three-step process was time-consuming due to subsequent treatment of by-products with potassium permanganate. In this communication, the nitrogen–nitrogen double bond was constructed in one step using electrochemical synthesis.

Organic electrosynthesis uses electrons as a driving force for reaction to take place, and its significant advantage[6] is that variation of electrode potential provides fine tuning of the reaction direction. Specifically, the construction of nitrogen double bonds on triazole groups by electroorganic synthesis requires constant current and control of potential window, which should simplify the procedure.[7] Electrochemically, 1,1′,2,2′-tetra-amino-5,5′-azo-1,3,4-triazole was obtained at 2.5 V and 5,5′-bitetrazole at 1.6 V.[8,9] Consequently, electrochemical organic synthesis could lead to azo structure by controlling the voltage window.

The electrosynthesis using electrons as channel[10] promotes activation of the reaction site of the substance through the potential window or rated current (acid and base additives or other redox components can be applied to modify the medium). Electroactivation of the reaction center group causes end-to-end linkage and followed by kinetically driven removal of hydrogen ions to create azo structure.[8] Thus, the reaction parameters can be adjusted to electrochemically activate the reaction site whereas hydrogen coupling is driven by the electrode material.

In our experiments, we used 3,5-diamino-1*H*-1,2,4-triazole **1** (0.495 g) as the substrate (Figure 1), carbon cloth as the positive electrode, platinum sheet as the negative electrode, Hg/HgO as reference electrode, 0.1 M NaOH was the supporting electrolyte. The control of the potential window (1.0 V) was performed with the Chi670E electrochemical workstation. To drive the process toward azo product (*cf*. ref. 11), the reaction time was controlled by monitoring the theoretical charge ($Q = 965$ C).[11] The Gaussian software[12] was used to optimize and estimate the energy of the formed azo product **2**, and its density value reached 1.72 g cm^{-3}. Using K–J equation,[13] the explosion heat was 7542.67 m s^{-1} and the burst pressure was 22.8579 GPa.

3,5-Diamino-1*H*-1,2,4-triazole **1** was homo-coupled under voltage window and power-on time control regimes. This compound has two C–NH$_2$ fragments with two active oxidation sites, however three oxidation peaks on the CV plot (carbon cloth as the working electrode, platinum sheet electrode as the counter electrode, Hg/HgO as the reference electrode, and sodium hydroxide as the supporting electrolyte) were observed at 0.928, 1.225 and 1.874 V [Figure 2(*a*)]. The oxidation potential of organic substrates usually reflects their reactivity and is a key factor in controlling product efficiency and side reactions.[14] At voltage windows of 1.0 and 1.5 V, color changes

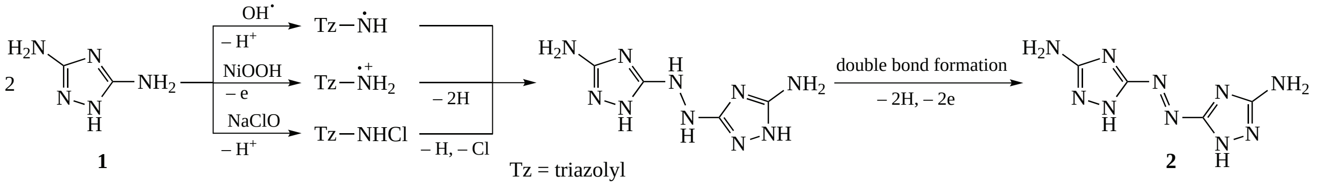


Figure 1 Reaction pathway diagram for 3,5-diamino-1*H*-1,2,4-triazole **1** under different electrolysis conditions.

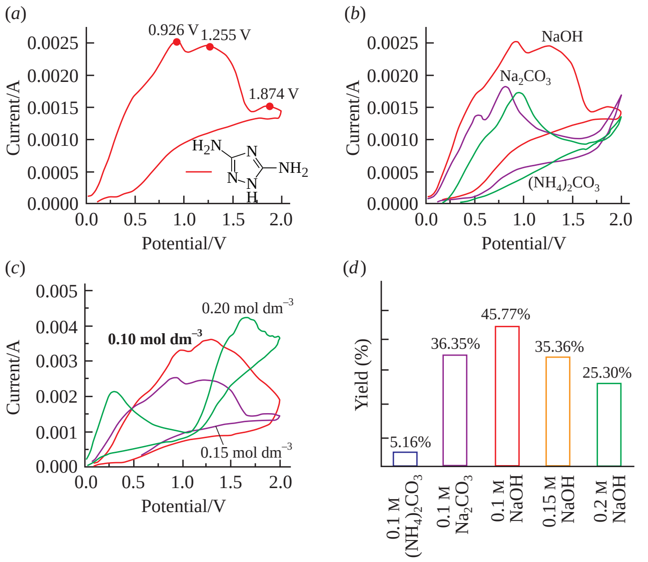


Figure 2 (*a*) Cyclic voltammetry (CV) curve of 3,5-diamino-1*H*-1,2,4-triazole **1**; (*b*) CV curves for **1** in different electrolytes; (*c*) CV curves for **1** at different concentrations of NaOH; (*d*) dependence of product **2** yield on electrolyte nature.

were found. The characterization of the products showed that the reddish-brown target 3,3′-diamino-5,5′-azo-1,2,4-triazole [5,5′-diazene-1,2-diylbis(3-amino-1*H*-1,2,4-triazole)] **2** was obtained at 1.0 V. Nevertheless, at 1.5 V odorous brown substances were generated, and compound **2** was not detected. The cyclic voltammetry study of authentic sample **2** revealed an oxidation peak at 1.442 V, which may be an oxidation potential of by-products at 1.5 V. The power-on time test was carried out at 1.0 V voltage, and before the theoretical charge of 2 F mol^{-1} was passed. As the power increased, it was observed that the color of the reaction mixture gradually changed from colorless to yellow and finally to dark red. After passing 3 F mol^{-1} electricity, the reaction stopped, the color changed from colorless to dark red, while target product **2** was detected. Apparently, 3,5-diamino-1*H*-1,2,4-triazole **1** selectively reacted under voltage control while azo product **2** was not stable in alkaline solution and could be further oxidized. Hence, all the following reactions were performed under 1.0 V voltage and the reaction time was guaranteed to be interrupted at the theoretical charge (Q_t = 2 F mol^{-1}, or Q/Q_t = 1).[15]

Different supporting electrolytes were tested and the electrolyte content was adjusted to gradually improve the yield. The experiments showed that the coupling of acidic azole was more likely to occur under alkaline conditions,[16] so supporting electrolytes with increasing alkalinity were used. Carbon cloth was used as the positive electrode, platinum sheet electrode was the counter electrode, and Hg/HgO was the reference electrode providing 1.0 V voltage[17] [Figure 2(*b*)], and azo products were generated under alkaline conditions. Among the supporting electrolytes with different alkalinity, sodium hydroxide was the most productive. Control experiment on the sodium hydroxide content showed that the yield of **2** was the highest when the NaOH/**1** ratio was 1 : 1. Most probably, deprotonation of the amino group with OH$^-$ anion was the activation step.[13] When the concentration of sodium hydroxide reached a certain value, bidirectional effect on C–NH_2 reached a threshold, either because of exceeding OH$^-$ attack at the second amino group or because of the decomposition of compounds in a strongly alkaline medium. Figure 2(*c*) shows that as the concentration increases, the polarization of the oxidation peak becomes more pronounced, and the oxidation voltage value would decrease. The dependence of the yield of azo product **2** on the electrolyte nature is shown in Figure 2(*d*).

Table 1 Dependence of 3,5-diamino-1*H*-1,2,4-triazole **1** electrolysis outcome on the electrode material.[a]

Anode	Cathode	Yield of **2** (%)
C	Pt	45.77
Pt	Pt	26.78
Ni	Pt	42.27
Cu	Pt	20.63

[a] Electrolyte 0.1 M NaOH (aq.), electricity passed 2 F mol^{-1}.

The influence of the electrode material (carbon, platinum, copper, and nickel) on the process outcome was also studied (Table 1). Based on the CV scans (Figure 3), it was found that the oxidation potential window of both the active and inactive electrodes was about 1.0 V, and the oxidation potential of the copper electrode was slightly shifted to the left. After electricity passing, the solution color changed from colorless to dark red. 5,5′-Diamino-3,3′-azo-1*H*-1,2,4-triazole **2** was generated with all electrode materials tested. However, the best yield of azo product **2** was obtained when carbon cloth was the cathode and inert platinum sheet was the anode, possibly because the carbon cloth had higher specific conductivity in alkaline medium and constant voltage.[18] Active nickel and copper electrodes were covered with black substances in the course of the electrolysis, with the yield of **2** in case of nickel being better.[19] This was mainly due to corrosion of copper during electrolysis forming a black oxidation product CuO_x on the surface of the electrode. The nickel electrode was also oxidized to produce NiO_2, however the increase in the current value was observed[20] during the process. Apparently, nickel electrode is involved in some other reactions in this process. The oxidized Ni^{2+} cation can be further oxidized into NiOOH[21] and NiO_2, while its reduction at the cathode should give Ni metal. Subsequently, tests were performed with $Ni(OH)_2$ and NiOOH, when the current values were 140 and 2 mA at 1.0 V, respectively. A large amount of NiO_2 was generated in the $Ni(OH)_2$ solution reaction cell, no azo product **2** formation was observed, and it was possible that $Ni(OH)_2$ had an inhibitory effect on the oxidation of 3,5-diamino-1*H*-1,2,4-triazole **1**. Small amount of azo product **2** was formed in the case of pre-prepared NiOOH electrode material. As an intermediate product of nickel hydroxide,[22] NiOOH has certain oxidation properties and can promote the oxidation reactions, and its electrophilic lattice oxygen can capture protons and electrons

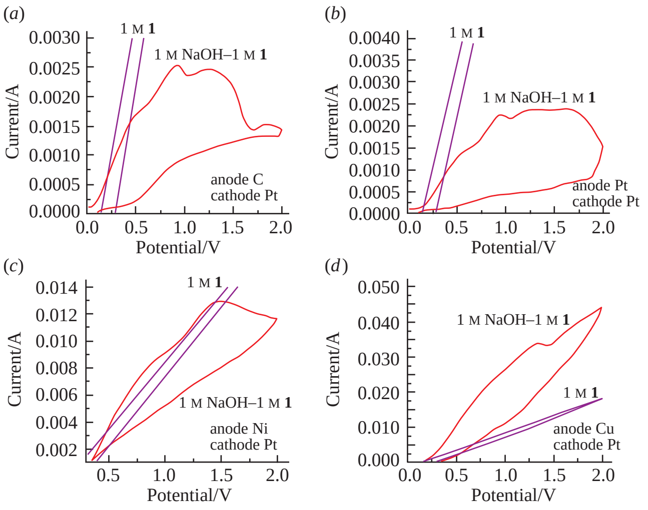


Figure 3 Cyclic voltammetry of compound **1** in the presence or in the absence of NaOH at (*a*) carbon anode, (*b*) platinum anode, (*c*) nickel anode, and (*d*) copper anode.

from primary amines in a proton-coupled electron transfer (PCET) process.[23] This may also contribute to the oxidative coupling of 3,5-diamino-1*H*-1,2,4-triazole **1**.

The resistance of unactivated amino group towards oxidation is generally average,[24] so direct electrochemical oxidation usually requires high potential (which also can be the reason for poor compatibility with other functional groups). To avoid these difficulties, the use of inert solvent and specific redox additives is suggested. The essence of redox media[25] lies in the activation of substrates, the incorporation of functional groups or the formation of bonds, which should improve reaction selectivity. Previous experiments proved that NiOOH promoted the dehydrogenation coupling of 3,5-diamino-1*H*-1,2,4-triazole **1**. Lyalin *et al*.[26] observed that NaClO oxidized 3-amino-1,4-dimethyl-1*H*-pyrazole to 1,2-bis(1,4-dimethyl-1*H*-pyrazol-3-yl)-diazene, so we supposed that NaClO should produce similar oxidative effect on 3,5-diamino-1*H*-1,2,4-triazole **1**. When NaCl and substrate **1** were added at the same time, no azo product **2** was found, possibly this substrate inhibited the production of Cl_2. In a two-step process, first NaCl as the supporting electrolyte was electrolyzed under a voltage window of 1.4 V until a certain amount of NaOCl was produced. Second, 3,5-diamino-1*H*-1,2,4-triazole **1** in a ratio of 3 : 1 was added, and the solution changed its color to dark red thus indicating formation of azo compound **2**.

The formation of N–N double bonds usually involves the interconnection of two reactive radical ions.[27] Since free radical ions have strong activity and short time-performance,[28] they are inferior to organic cations and anions in reactivity. For this reason, the appropriate redox medium should be selected to conform the *in situ* surface structure or electrophilic lattice oxygen to achieve efficient oxidation of organic substrates.[27,29] This may help to avoid the limitations in the kinetic conversion process, facilitate the overall charge migration in the system, and improve the transition of the medium from heterogeneous phase (solid–liquid phase) to homogeneous one (liquid phase). Figure 1 shows the possible mechanism of 3,5-diamino-1*H*-1,2,4-triazole **1** conjugation. Whether it was NaOH, NiOOH or NaOCl, it was a clean and green way to obtain the coupling product **2**. The mode of action could be divided into three types: (*1*) extraction of hydrogen atoms from amino groups with hydroxide radicals, (*2*) direct oxidation mode of action of lattice oxygen of NiOOH, and (*3*) indirect halogenated hydrogenation with sodium hypochlorite as a halogenating agent.

The activity of substrates is usually directly expressed at the oxidation potential (E_P^ox);[23] the $E_\mathrm{P}^\mathrm{ox} = 0.9225$ V for sodium hydroxide lies between NiOOH ($E_\mathrm{P}^\mathrm{ox} = 0.75$ V) and NaClO ($E_\mathrm{P}^\mathrm{ox} = 1.225$ V). However, the use of sodium hydroxide seems the most direct way, which could maximize the reaction outcome when the product yield was the highest. May be the alkaline medium is good for hydrogen evolution and oxidation reactions, so OH^- anions make the removal of hydrogen cations from amino groups easier. The oxidation potential under NiOOH conditions was advanced by 0.178 V, indicating that the coupling of the unique electrophilic lattice oxygen to amino groups would cause strong activation, and the formation of OH_{ad}–$(H_2O)_x$–NiPt compounds in solution had a certain promoting effect on hydrogen evolution and oxidation reactions.[30] At the same time, the formation of the poorly soluble nickel oxide NiO_2 at a continuous voltage caused the electrode to be covered, thus retarding the reaction. The mechanism of action of NaClO included change of its reactivity through electron migration,[31] showing the advantage of organic electrochemical *in situ* redox. First, NaClO was continuously produced at the working electrodes followed by hydrolysis to generate more stable HOCl. However, due to little NaClO amount obtained from NaCl, the reaction rate was low, and the production of chlorine gas caused by triazole was very small. Moreover, the halide agent was not effective for the removal of hydrogen ions from amino groups compared with $OH^{\bullet-}$ radical anions. In summary, 3,5-diamino-1*H*-1,2,4-triazole **1** was suitable for treatment with hydroxide, nickel hydroxyoxide and sodium hypochlorite, and azo product **2** could be obtained under all three conditions.

In conclusion, 3,5-diamino-1*H*-1,2,4-triazole **1** was subjected to oxidative electrolysis at specified low voltage potential window to selectively produce 5,5′-diamino-3,3′-azo-1*H*-1,2,4-triazole **2**. The proper choice of electrode materials and medium allows one to achieve good yield of the product **2** at nearly 2 F mol^{-1} electricity passed.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.040.

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