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Communication—Electrosynthesis of Isonicotinic Acid via Indirect Electrochemical Reduction of Pyridine in the Presence of CO_2

Kobra Ghobadi, Hamid R. Zare,[z] Hossein Khoshro, and Alireza Gorji

Department of Chemistry, Yazd University, Yazd 89195-741, Iran

The electrocatalytic reduction of CO_2 by Schiff base of N, N′-bis(3-hydroxy-2-naphthaldehyde)-1,3-phenylenediimino (NMPD) was studied in an acetonitrile solvent and at room temperature. Indirect electrocatalytic activity of NMPD for reduction of pyridine was empirically demonstrated. It is rational, to view electrocatalytically activated CO_2, $CO_2^{\bullet-}$, with a dual activity toward pyridine. The spectral characteristics of the coulometric product indicated that isonicotinic acid is the final product of pyridine reduction in the presence of NMPD and CO_2.

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Using CO_2 in the synthesis of organic compounds has received considerable attention. In spite of CO_2 being as the most abundant, nontoxic, and inexpensive resource, the large overpotential required for CO_2 conversion leads to a low efficiency of recycling this molecule into useful products.[1] Hence, finding catalysts to decrease this high overpotential and to increase the selectivity of reduction processes has become an important concern. For this purpose, a number of transition metal complexes[2] and some organic compounds, like substituted benzenes[3] and benzil,[4] have been used.

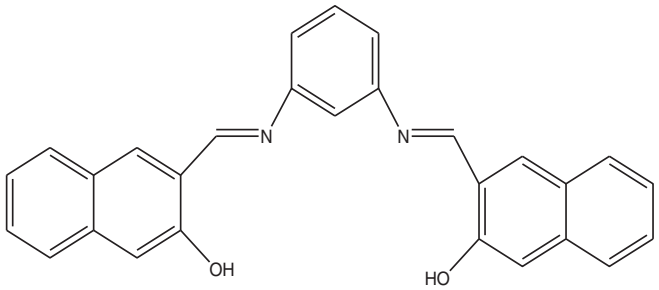
This paper focuses on the electrocatalytic reduction of CO_2 by Schiff base of N, N′-bis(3-hydroxy-2-naphthaldehyde)-1,3-phenylenediimino (NMPD). Isonicotinic acid was synthesized as the product of indirect reduction of pyridine in the presence of CO_2 and NMPD electrocatalyst. Also, it was shown that the reduction product of CO_2 has a dual activity for the synthesis of isonicotinic acid by an EC′C′CC mechanism. As reported in the literature, isonicotinic acid has been used as a photosensitive resin stabilizer, an electroplating additive and an anticorrosion reagent.[5] Also, this compound is used in the synthesis of some pharmaceuticals, such as nialamide (an antidepressant) and terefenadine (an antihistamine).[6] Oxidation of 4-picoline and hydrolysis of 4-cyanopyridine[7] are two conventional chemical processes for isonicotinic acid synthesis. In this work, it was shown NMPD has electrocatalytic activity for CO_2 reduction. Also the produced $CO_2^{\bullet-}$, can be used to electrosynthesis of isonicotinic acid.

Experimental

Chemicals and apparatus.—The Schiff base of N, N′-bis(3-hydroxy-2-naphthaldehyde)-1,3-phenylenediimino, NMPD, (Scheme 1) was prepared as reported in the literature.[8] All the reagents had analytical grades and were purchased from Merck Company and used without any further purification. Acetonitrile was used as a solvent. CO_2 and Ar had a purity of 99.995%.

Cyclic voltammetry was performed using an EG&G PARSTAT 2273 equipped with a Power Suite software in a conventional three-electrode electrochemical cell containing a glassy carbon electrode (GCE) with a diameter of 2 mm as the working electrode, Ag/Ag^+ (0.01 M $AgNO_3$ in a 0.1 M tetrabutylammonium perchlorate (TBAP), acetonitrile solution) as the reference electrode, and a Pt wire as the counter electrode. Controlled potential coulometry (CPC) was carried out using a SAMA 500 electroanalyzer system in an undivided glass cell equipped with a gas inlet and outlet with a graphite rod as the cathode, a platinum plate (ca. 5 cm^2) as the anode, and Ag/Ag^+ (0.01 M $AgNO_3$ in 0.1 M TBAP acetonitrile solution) as the reference electrode. Fourier transform infrared (FTIR) spectrum analysis was performed on an EQUINOX55 spectrometer. ^1H and ^{13}C NMR were measured on a DRX-400 (Bruker) spectrometer with $CDCl_3$ as a solvent in the presence of $SiMe_4$ as an internal standard. All the measurements were performed at room temperature.

[z]E-mail: hrzare@yazd.ac.ir



Scheme 1. Structure of Schiff base of N,N′-bis(3-hydroxy-2-naphthaldehyde)-1,3-phenylenediimino, NMPD.

Electrolysis procedure.—CPC was used in 40.0 mL acetonitrile containing 0.1 mM TBAP and 0.1 mmol NMPD as a catalyst in the presence of 1.0 mmol of pyridine. Prior to every experiment, the solution was bubbled with Ar gas for 20 minutes. CO_2 was continuously bubbled into the solution during the electrolysis and a constant potential of −2.0 V was applied to the working electrode. The results showed that pyridine conversions were about 100% after passing 2.9 F mol^{-1} of the starting compound (pyridine) at room temperature. The determined yield of isonicotinic acid was about 75%. At the end of the electrolysis, the solvent was completely removed, and the residue was dissolved in diethyl ether and filtered (5 × 20 mL). After separation of the isonicotinic acid product, it was characterized by FTIR, ^1H and ^{13}C NMR. The spectral characteristics of isonicotinic acid were obtained as follow: ^1H NMR ($CDCl_3$, 400 MHz): δ 7.43 (d.d, 2H, j = 3.2), δ 7.62 (d.d, 2H, j = 3.2), δ 11.03 (s, ^1H, CO_2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 128.09, 130.95, 132.39, 167.79 ppm; FTIR: 1714 (C=O), 1095, 1217 (C-O), 3380 (O-H).

Results and Discussion

Electrosynthesis of isonicotinic acid by indirect electrocatalytic reduction of pyridine in the presence of CO_2.—Voltammograms (a), (b) and (c) of Fig. 1 are the cyclic voltammograms of the working electrode in an acetonitrile solution containing 0.1 M TBAP and 1.0 mM pyridine (voltammogram a), 1.0 mM NMPD (voltammogram b) and 1.0 mM pyridine + 1.0 mM NMPD (voltammogram c). The experimental results indicate that the cyclic voltammograms of the saturated solution of CO_2 and also 1.0 mM pyridine solution which is saturated with CO_2 are exactly same as voltammogram (a). Consequently, solutions containing pyridine alone, saturated solution of CO_2, or 1.0 mM pyridine which is saturated with CO_2 are inactive electrochemically in the potential range of −1.0 to −2.6 V, pyridine cannot be reduced by NMPD, and also NMPD only consists of one cathodic peak at the potential of −2.03 V that is related to the reduction of imine bond and the formation of its radical anion as shown in reaction 1.[9] Voltammogram (d) corresponding to 1.0 mM NMPD solution in the presence of CO_2. The current response of voltammogram (d) indicates

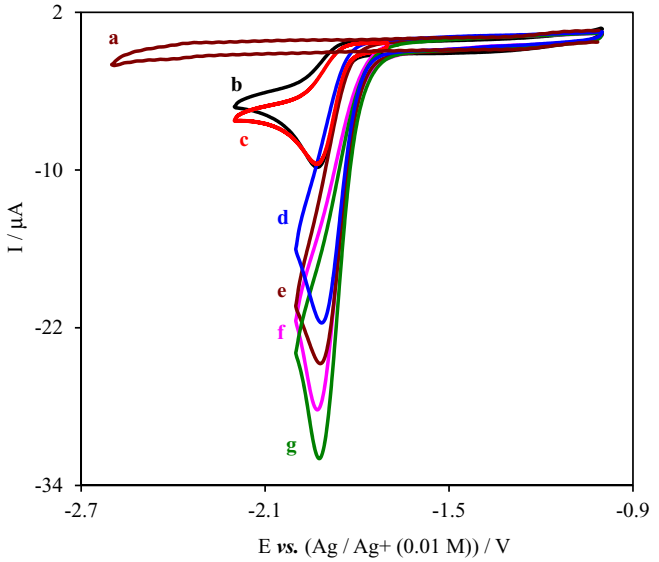


Figure 1. Cyclic voltammograms of a glassy carbon electrode in an acetonitrile solution containing 0.1 M TBAP and (a) 1.0 mM pyridine, (b) 1.0 mM NMPD, (c) 1.0 mM pyridine + 1.0 mM NMPD, (d) 1.0 mM NMPD in the presence of CO_2. (e), (f) and (g) as (d) in the presence of 1.0, 2.0 and 3.0 mM pyridine respectively. Potential scan rate: 100 mV s^{-1}.

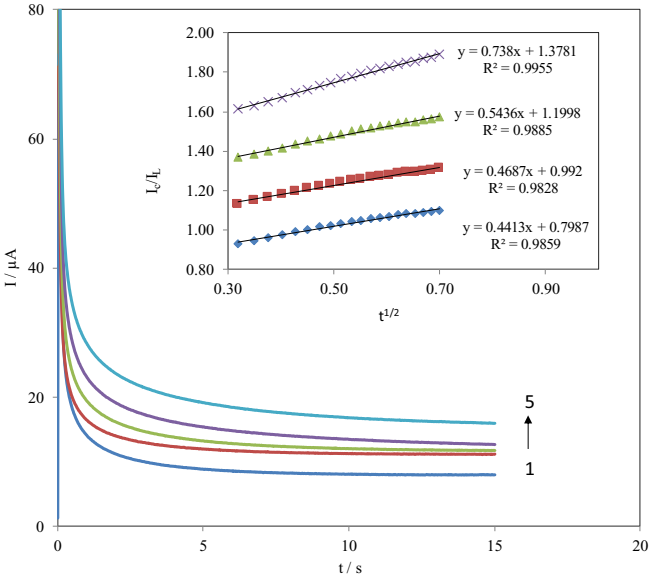


Figure 2. Chronoamperograms of a glassy carbon electrode in an acetonitrile solution containing 0.05 M TBAP, 1.0 mM NMPD and (a) saturated with CO_2, (b), (c), (d) and (e) as (a) in the presence of 0.2, 0.3, 0.5, 0.7 mM pyridine, respectively. Inset shows plots of I_C/I_L vs. $t^{1/2}$ obtained from chronoamperograms 1–5.

that the reduction peak current of the NMPD increases dramatically in the presence of CO_2. Also, a comparison voltammograms of (a) and (d) indicates the overpotential decrease of CO_2 reduction in the presence of NMPD is more than 500 mV. These results are indicative of electrocatalytic reduction of CO_2 to $CO_2^{\bullet-}$, regeneration of NMPD and, finally, its participation in the electrocatalytic cycle according to reactions 1 and 2.[10]

$$NMPD + e \rightarrow NMPD^{\bullet-} \quad (E) \qquad [1]$$

$$NMPD^{\bullet-} + CO_2 \rightarrow NMPD + CO_2^{\bullet-} \quad (C') \qquad [2]$$

Also, the voltammetric results show a significant rise in the electrocatalytic cathodic peak current with an increase of CO_2 concentration in the solution. This result is further proof for the electrocatalytic activity of NMPD in reduction of CO_2. Voltammograms (e), (f) and (g) of Fig. 1 are the cyclic voltammograms of acetonitrile (0.1 mM TBAP) solutions containing 1.0 mM NMPD, CO_2 and different concentrations of 1.0, 2.0 and 3.0 mM of pyridine, respectively. The dependence of the cathodic peak current on the concentration of pyridine proves that $CO_2^{\bullet-}$ serves as an electron transfer mediator, or a catalyst, for pyridine reduction (reaction 3).[11] In other words, electron transfer from $CO_2^{\bullet-}$ to the aromatic ring leads to production of radical anions of pyridine, $Py^{\bullet-}$, as shown in reaction 3.[11,12] A comparison of the gradual increase of the electrocatalytic current of the CO_2 reduction by NMPD in the presence of pyridine (voltammograms e-g) with the electrochemical reduction of NMPD in the presence of pyridine (voltammogram c) as well as the electrocatalytic reduction of CO_2 in the presence of NMPD (voltammogram d) indicates that pyridine is indirectly reduced by electrocatalytically activated CO_2 in the presence of NMPD, as shown in reaction 3.

$$Py + CO_2^{\bullet-} \rightarrow Py^{\bullet-} + CO_2 \quad (C') \qquad [3]$$

Chronoamperometry was employed to evaluate the electron transfer catalytic rate constant, k, for the reaction between pyridine and $CO_2^{\bullet-}$ (Fig. 2). The variation of I_C/I_L versus $t^{1/2}$ for different concentration of pyridine is shown in Fig. 2, inset. I_C is the catalytic current of pyridine in the presence of CO_2 and NMPD and I_L is the limited current in the absence of pyridine. The value k of the catalytic process can be obtained from the slope of these plots according to the reduced form of the Galus equation.[13] The calculations indicate the average value of k is 244.4 ± 50.5 M^{-1} S^{-1}.

In order to confirm the final product of pyridine reduction in the presence of $CO_2^{\bullet-}$ and NMPD, controlled potential coulometry, CPC, was performed at −2.0 V as described in the Experimental section. Then, the coulometric product was separated and characterized by FTIR, ^1H and ^{13}C NMR spectroscopy. The spectral characteristics of the coulometric product (not shown) indicate that isonicotinic acid is a final product of pyridine reduction in the presence of CO_2 and NMPD. In other words, the spectral characteristics of the coulometry product indicate that $Py^{\bullet-}$ is coupled with $CO_2^{\bullet-}$ and, thus, the final product of coulometry is dianion of isonicotinic acid, $PyCOO^{2-}$, as shown in reactions 4. It is noted, the coulometry experiment was performed under CO_2 atmosphere and in the absence of O_2. After electrolysis, the solution was exposed under air. As a result, the product of isonicotinic acid is obtained from the oxidation of $PyCOO^{2-}$ by dissolved O_2 in the analyte solution according to reaction 5.

$$Py^{\bullet-} + CO_2^{\bullet-} \rightarrow PyCOO^{2-} \quad (C) \qquad [4]$$

$$PyCOO^{2-} \xrightarrow{-2e} PyCOOH \quad (C) \qquad [5]$$

Therefore, the reaction of pyridine with CO_2 in the presence of NMPD follows an EC′C′CC mechanism (reactions 1–5), and the final product is isonicotinic acid. This mechanism and the final product is same as those reported in our previous work.[11] However, more solubility and also, easier synthesis of the mediator, NMPD, respect to the other catalysts such as the Ni(II) complex are advantages for this work.[11] In addition, CPC results indicate that diminution of the current during the electrolysis, in the presence of NMPD is significantly less than that observed for the Ni(II) complex. This observation demonstrates more stability of NMPD respect to the Ni(II) complex as an electron transfer mediator for reduction of CO_2.

Conclusions

In the present study, we have provided evidence for electrocatalytic reduction of CO_2 by Schiff base of N,N-bis(3-hydroxy-2-naphthaldehyde)-m-phenylenediamine, NMPD, as an excellent electrocatalyst. The voltammetric results indicate that the reduction

product of CO_2, $CO_2^{\bullet-}$, in the presence of NMPD serves as a mediator to reduce pyridine. The spectral characteristics of FTIR, ^1H and ^{13}C NMR of the coulometry product have proved that isonicotinic acid is the final product of indirect electrocatalytic reduction of pyridine in the presence of NMPD and CO_2.

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