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Dual activity of electrocatalytic activated CO₂ toward pyridine for synthesis of

isonicotinic acid: An EC'C'C mechanism

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Abstract

The present study demonstrates the indirect electrocatalytic synthesis of isonicotinic acid using a Ni complex, $[Ni^{II}(Me_4-(NO_2Bzo)_2[14]tetraeneN_4)]$, in an acetonitrile solution at room temperature. The complex was used as an excellent electrocatalyst for the reduction of carbon dioxide. The results indicate that the electrocatalytic reduction product of CO_2 (CO_2^{-}) has a dual role in the electrosynthesis of isonicotinic acid. The dual activity of CO_2^{-} involved indirect electrocatalytic reduction of pyridine as well as its radical reaction with pyridine radical anion to form isonicotinic acid. Finally, EC'C'C mechanism was proposed for the synthesis of isonicotinic acid. In contrast, the reaction of pyridine with CO_2 in the absence of the complex follows an EC'C mechanism, and the final product is 4,4'-bipyridine.

Keywords: Carbon dioxide, Pyridine, Isonicotinic acid, Bipyridine, Nikel (II) complex

1. Introduction

The transformation of CO₂, as an ideal C1 source, to useful organic compounds is of great interest and importance [1, 2]. The ability of carbon dioxide to promote the reduction of organic substrates has been reported in the literature [3, 4]. In the case of pyridine, which is reduced at potentials more negative than CO₂, the radical anion CO₂[•] promotes the conversion of pyridine into 4,4'-bipyridine [4]. Owing to the thermodynamically and kinetically stability of CO₂ [5], a number of transition metal complexes have been extensively employed as homogeneous catalysts for the electrochemical reduction of CO_2 [6-9]. As this paper is concerned, in the field of carbon-carbon bond formation using carbon dioxide, a Ni complex, [Ni^{II}(Me₄- $(NO_2Bzo)_2[14]$ tetraeneN₄)], was used for indirect electrocatalytic synthesis of isonicotinic acid from CO₂ and pyridine in an acetonitrile solution. The complex was used as an excellent electrocatalyst for reduction of CO_2 . The electrocatalytic reduction product of CO_2 (CO_2) has a dual role in the electrosynthesis of isonicotinic acid. The dual activity of CO₂^{•-} involved at first pyridine indirect electrocatalytic reduction and then its radical reaction with pyridine radical anion to form isonicotinic acid. Finally, EC'C'C mechanism was proposed for synthesis of isonicotinic acid. Isonicotinic acid is used in the synthesis of some pharmaceutically important drugs such as isoniazid (an antituberculostatic drug), terefenadine (an antihistamine) and nialamide (an antidepressant) [10, 11]. Isonicotinic acid is also used for the synthesis of inabenfide (a plant growth regulator). Furthermore, isonicotinic acid has emerged as an anticorrosion reagent, an electroplating additive and a photosensitive resin stabilizer [12].

2. Experimental

2.1. Chemicals and apparatus

A Ni (II) complex, $[Ni^{II}(Me_4-(NO_2Bzo)_2[14]tetraeneN_4)]$, was prepared as previously described [13]. All the other chemicals were of analytical reagent grades, purchased from Merck Company and used without any further purification. Argon (Ar) and CO₂ had a purity of 99.995% and were used directly.

Cyclic voltammetry was carried out 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) as a working electrode, a Pt wire as a counter electrode, and Ag/Ag^+ (0.01 M AgNO₃ in a 0.1 M TBAP acetonitrile solution) as a reference electrode. Controlled potential coulometry was performed using a SAMA 500 electroanalyzer system in an undivided glass cell equipped with a gas inlet and an outlet with a graphite rod as the cathode, a platinum plate (ca.6 cm²) as the anode and Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TBAP acetonitrile solution) as a reference electrode. ¹H and ¹³C NMR were measured on a DRX-400 (Bruker) spectrometer with CDCl₃ as a solvent in the presence of SiMe₄ as an internal standard. Fourier transform infrared (FTIR) spectrum analysis was performed on an EQUINOX55 spectrometer.

2.2. Typical electrolysis procedure

The electrolysis was carried out in 50.0 mL ACN containing 0.1 mol L⁻¹ TBAP, 2.0 mmol of pyridine, and CO_2 in the absence and the presence of 0.1 mmol L⁻¹ Ni (II) complex as a catalyst. Prior to every experiment, the solution was bubbled with Ar gas for 30 minutes. In controlled potential coulometry, constant potentials of -1.75 V and -2.4 V were applied to the working electrode in the presence and the absence of the Ni complex, respectively. The results showed

that the pyridine conversions were about 100% after passing 2.5 and 3.0 F mol⁻¹ of the starting substrate (pyridine) in the presence and the absence of the Ni complex at room temperature, respectively. At the end of the electrolysis, the solvent was removed under reduced pressure, and the residue was extracted with diethyl ether (4×25 mL). After evaporation of the ether, the crude product was characterized by FTIR, ¹H, and ¹³C NMR.

The spectral characteristics of the products were determined as follows (see Figs. S1 – S6 of Supplementary Information): isonicotinic acid: ¹H NMR (CDCl₃, 400 MHz): δ 7.47 (d.d, 2H, *j*=3.2), δ 7.66 (d.d, 2H, *j*=3.2), δ 7.95 (s, 1H, CO₂H), ¹³C NMR (CDCl₃, 100.6 MHz): δ 128.72, 130.83, 132.41, 167.63 ppm, IR: 3379 cm⁻¹(O-H), 1714, 1665 (C=O), 1590 (C=C), 1095 (C-O); 4,4'-bipyridine: ¹H NMR (CDCl₃, 400 MHz): ¹H NMR: 7.48 (d, 4H, *j*= 6), 8.68 (d, 4H, *j*= 5), ¹³C NMR (CDCl₃, 100.6 MHz): δ 121.44, 145.57, 150.67 ppm; FT-IR: 1696, 1653 cm⁻¹(C=N), 1578, 1555 cm⁻¹ (C=C), 1453, 1248, 1085 and 756 cm⁻¹.

3. Results and discussion

3.1. Indirect electrochemical reduction of pyridine by the Ni (II) complex

Voltammograms of (a) and (b) of Fig. 1 show the voltammetric responses of the GCE in the potential range of -0.7 to -2.6 V in an ACN (0.1 M TBAP) solution containing pyridine and CO₂, respectively. As shown, there is no redox peak in the presence of 1.0 mM pyridine (voltammogram a), which indicates that the reduction potential of pyridine does not take place even by applying -2.6 V. A weak cathodic current is started at about -2.3 V in the supporting solution containing CO₂ (voltammogram b) and its current remained unchanged during repetitive scans. Above results indicate that the cathodic charge of GC and its following carboxylation are not favored under working conditions [14]. This is likely due to using the supporting electrolyte

with more bulky tetraalkylammonium cation of TBA⁺ [14]. So, the reduction of carbon dioxide to the anion radical CO₂⁻ is a predominant electrode reaction in comparison with the chemical carboxylation of GC [14-16]. As previously reported, the cyclic voltammogram of 1.0 mM Ni (II) complex shows a one-electron redox couple with a formal potential $(E^{0'})$ of -1.65 V (voltammogram c) [17]. Voltammogram (d) shows the cyclic voltammogram of the Ni (II) complex solution in the presence of 1.0 mM pyridine. A comparison of voltammograms (c) and (d) indicates that there is no interaction between pyridine and the complex. Voltammogram (e) shows the voltammetric response of the supporting electrolyte containing the complex and CO₂. As it can be seen, the reduction peak current of the complex increases significantly in the presence of CO₂ while the anodic peak disappears. These results are due to the electrocatalytic reduction of CO_2 to CO_2^{-} by the complex (Eqs. 1 and 2) [17]. Voltammograms (f), (g) and (h) show the cyclic voltammograms of a 1.0 mM complex solution in the presence of CO₂ containing 1.0, 2.0 and 3.0 mM of pyridine, respectively. A comparison of voltammogram (e) and voltammograms (f)-(h) indicates that the cathodic peak current rises markedly with an increase of pyridine concentration in the solution containing the complex and CO₂. It is noted that, compounds with reduction potentials both lower and higher than CO₂, can enter into the carboxylation process [4, 17, 18]. It is clear that in both cases a radical-anion is formed in the initial event either from the substrate or from the CO₂ [4, 17, 18]. Considering the lack of electrocatalytic activity of the complex for reduction of pyridine, it is logical to conclude that the CO₂ activated by the complex promotes the reduction of pyridine. In other words, the initial process in carboxylation of pyridine is the formation the electroactivated CO_2 (CO_2) in the presence of the Ni complex. The increase of the reduction peak current in the presence of pyridine may be explained by an electron transfer from CO_2^{-1} to the aromatic ring leading to the

radical anion of pyridine and regeneration of CO_2 according to Eq. (3). The radical anion of pyridine produced in Eq. (3) may undergo different reactions such as coupling to radical anion CO_2^{-1} to form isonicotinic acid (Eq. 4) or coupling to another pyridine radical anion to give a dimer of 4,4'-bipyridine (Eq. 5) [4]. The spectral characteristics of the electrolysis product (section 2.2) indicate that the final product is isonicotinic acid. Observation of isonicotinic acid as the final product during the electrolysis of a solution containing pyridine and CO_2 in the presence of the Ni (II) complex can be rationalized by coupling of CO₂⁻⁻ with the radical anion of pyridine followed by oxidation intermediate (reaction 4). Therefore, an EC'C'C mechanism can be proposed for the reaction of pyridine with CO_2 in the presence of the complex as shown in reactions (1)-(4). In other words, a dual reactivity of the CO_2 radical anion toward pyridine, i.e. one-electron reduction of pyridine as a result of an electron transfer from the CO_2^{-} to pyridine (reaction 3) and radical addition of CO₂⁻ to the radical anion of pyridine (reaction 4), has a decisive role in the process of electrosynthesis of isonicotinic acid. Voltammograms (i), (j) and (k) of Fig. 1 show the cyclic voltammograms of the supporting electrolyte solution containing 1.0, 2.0 and 3.0 mM of pyridine, respectively, and CO₂ in the absence of Ni (II) complex. The increase of the reduction current with gradual addition of pyridine concentration and in the presence of CO_2 indicates that CO_2 has a direct key role as a promoter in the reduction of pyridine under these conditions. Moreover, a comparison of voltammogram (i) and (f) shows that the overpotential for reduction of pyridine in the presence of the complex decreases more than 600 mV. These results suggest that Ni (II) complex has an excellent indirect electrocatalytic effect for reduction of pyridine.

3.2. Synthesis of isonicotinic acid by catalytic reduction of pyridine in the presence the Ni (II) complex

In order to confirm the electrocatalytic behavior of the Ni (II) complex for the synthesis of isonicotinic acid, controlled potential coulometry was carried out at -1.75 V in a CO₂ saturated solution in the presence of pyridine and the Ni (II) complex as described in section 2.2. Also, to ascertain the possible synthesis of isonicotinic acid in the absence of the Ni (II) complex, controlled potential coulometry of ACN-0.1 M TBAP containing pyridine and CO₂ was performed at -2.4 V where reductions of CO₂ could take place in the absence of the Ni (II) complex. At the end of the electrolysis, the solutions were treated as mentioned in the experimental section. A yield of 90% of isonicotinic acid was achieved in the presence of the complex while, in its absence, a yield of 80% of 4,4'-bipyridine was reached. Produce of 4,4'bipyridine in the absence of the complex is a sign of coupling two radical anions of pyridine according to Eq. (5) [4]. Consequently, the reaction of pyridine with CO_2 in the absence of the complex follows an EC'C mechanism, and the final product is 4,4'-bipyridine [4]. The mechanism is proposed to include a one-electron reduction of CO_2 (E) followed by reaction (3) (C) and finally a chemical reaction of two pyridine radical anions and then oxidation of produced intermediate to give 4,4'-bipyridine (reaction 5) (C) [4]. The significant increase of the cathodic peak current of the complex in the presence of CO₂ (voltammogram e) as compared to that in the presence of CO₂ alone (voltammogram b) indicates that the kinetic of production of CO_2 in the presence of the complex is faster than that in its absent. So, production of isonicotinic acid instead of 4,4'-bipyridine may be due to more concentration of CO₂⁻ in the presence of the complex. In other words, in the presence of the complex, radical addition of CO_2 to the radical anion of pyridine occurs preferentially to form isonicotinic acid.

$$\begin{bmatrix} \text{Ni} (\text{II}) \text{ complex} \end{bmatrix} + e \implies [\text{Ni} (\text{I}) \text{ complex}]^{-1} (\text{E}_{q}) (1)$$

$$\begin{bmatrix} \text{Ni} (\text{I}) \text{ complex} \end{bmatrix}^{-1} + CO_{2} \implies [\text{Ni} (\text{II}) \text{ complex}] + CO_{2}^{-1} (C_{i}^{-1}) (2)$$

$$\begin{bmatrix} \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}^{-1}) (3) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}^{-1}) (3) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (4) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (4) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (4) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (5) \\ \text{Ni} + CO_{2}^{-1} + CO_{2} & (C_{i}) (C_{i})$$

4. Conclusions

The present study demonstrates the dual reactivity, one-electron transfer and radical addition of $CO_2^{\bullet-}$ toward pyridine in the presence of $[Ni^{II}(Me_4-(NO_2Bzo)_2[14]tetraeneN_4)]$ complex. The pyridine radical anion is produced from the reaction of $CO_2^{\bullet-}$ (as an electron transfer) with pyridine. Also, the radical addition of $CO_2^{\bullet-}$ to the radical anion of pyridine takes place in the presence of the Ni complex to form isonicotinic acid. In contrast, 4,4'-bipyridine is produced as a result of coupling the radical anions of pyridine in the absence of the complex. It is noteworthy that the reduction potential of CO_2 is significantly less negative in the presence of the complex. Consequently, Ni (II) complex has an excellent indirect electrocatalytic effect for reduction of pyridine with a diminution of the overpotential about 600 mV. Finally, EC'C'C mechanism is proposed for synthesis of isonicotinic acid.

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Legends of Schemes and Figures

Scheme 1. Structure of [Ni^{II}(Me₄-(NO₂Bzo)₂[14]tetraeneN₄)] complex.

Fig. 1. Cyclic voltammograms of a glassy carbon electrode in an ACN (1.0 M TEAP) solution (a) after addition of 1.0 mM pyridine, (b) in the presence of CO_2 , (c) after addition of 1.0 mM Ni (II) complex, (d) as (c) after addition of 1.0 mM pyridine, (e) as (c) after addition of CO_2 , (f)-(h) as (e) after addition of 1.0, 2.0 and 3.0 mM pyridine respectively and (i)-(k) as (b) after addition of 1.0, 2.0 and 3.0 mM pyridine, respectively. Scan rate: 100 mV s⁻¹.

Scheme 1



Fig. 1



E vs. (Ag / Ag⁺ (0.01M)) / V

Graphical abstract



Highlights:

A Ni complex was used for indirect electrocatalytic synthesis of isonicotinic acid from carbon dioxide and pyridine.

The results indicate that the electrocatalytic reduction product of CO_2 (CO_2^{-}) has a dual role in the electrosynthesis of isonicotinic acid.

An EC'C'C mechanism was proposed for synthesis of isonicotinic acid.

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