



The effect of electronic structure on electrocatalytic behaviors of cobalt Schiff base complexes: Electrosynthesis of 2-phenylacetic acid using carbon dioxide



Hossein Khoshro, Hamid R. Zare*, Alireza Gorji, Mansoor Namazian, Abbas A. Jafari, Rasoul Vafazadeh

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

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ABSTRACT

Electrochemical fixation of carbon dioxide was used as an efficient method to synthesize 2-phenylacetic acid. The electrochemical carboxylation of benzyl bromide by two cobalt Schiff base complexes of [N,N'-bis(salicylaldehyde)-1,2-phenylenediimino cobalt(II)], [Co(II) salophen], and [N,N'-bis(benzoylacetone) ethylenediimino cobalt(II)], [Co(II) bzaen], in N,N-dimethylformamide and in the presence of carbon dioxide was investigated using cyclic voltammetry method. The electrocatalytic reduction mechanism of benzyl bromide is dependent on the electronic structure of the complexes. Moreover, the presence of CO₂ improves the catalytic efficiency and stability of the complexes. Finally, controlled potential coulometry (CPC) and constant current coulometry (CCC) were carried out in the absence and the presence of CO₂. The electrosynthesis yields of 2-phenylacetic acid from benzyl bromide are obtained by 50% and 55% using CPC and 60% and 70% using CCC under mild conditions using [Co(II) salophen] and [Co(II) bzaen] complexes respectively. DFT calculations along with Mulliken/NBO studies have been carried out, in order to support the experimental results.

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1. Introduction

Global warming caused by increasing emissions of greenhouse gases, mainly carbon dioxide, has become a serious environmental problem. Carbon dioxide is an ideal C1 source due to its natural abundance, low cost, no toxicity, and good potential as a renewable source [1]. Therefore, chemical fixation of CO₂ into an organic substance has received much attention recently [2]. One of the most promising methodologies in this area is the synthesis of carboxylic acids via the electrochemical carboxylation of organic halides [3–8]. A major drawback of this method is that the direct electrochemical reduction of organic halides often occurs at rather negative potentials where concomitant reduction of CO₂ leads to undesired products such as oxalate, carbonate and formate, as well as to a reduced current efficiency [9]. Therefore, making efforts to find catalysts able to decrease the high overpotential and to increase the selectivity of the reductive process has become a main challenge. Transition metal complexes play a very important role in many electrochemical catalytic processes [10]. In particular, cobalt complexes containing tetradentate Schiff base ligands have

been recognized as powerful catalysts in the electrochemical reduction of electrophiles such as organic halides [4,11,12].

The aim of this paper is to study the catalytic activities of two [Co(II) salophen] and [Co(II) bzaen] complexes (see Scheme 1 for structures) for the reduction of benzyl bromide and benzyl chloride in N,N-dimethylformamide (DMF). The paper also reports the mechanism of benzyl halides electrocatalytic reduction by these complexes. In addition, efficiency of the method for electrocarboxylation of benzyl bromide is studied under mild conditions.

The conversion rate of 100% was achieved for both complexes. Also, the chemical yields of 2-phenylacetic acid from benzyl bromide were obtained by 50% and 55% using controlled potential coulometry and 60% and 70% using constant current coulometry using [Co(II) salophen] and [Co(II) bzaen], respectively.

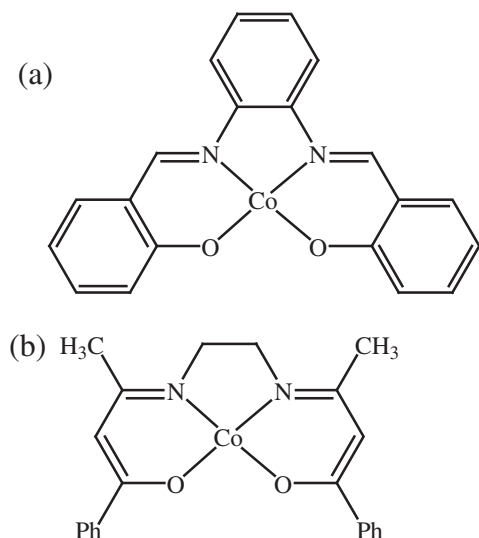
2. Experimental

2.1. Chemicals and apparatus

[N,N'-bis(salicylaldehyde)-1,2-phenylenediimino cobalt(II)], [Co(II) salophen], and [N,N'-bis(benzoylacetone) ethylenediimino cobalt(II)], [Co(II) bzaen], complexes were prepared as previously described [13,14]. Briefly, for the synthesis of [Co(II) salophen] complex, at the first, the tetradentate Schiff base ligand of

* Corresponding author. Tel.: +98 351 8122669; fax: +98 351 8210991.

E-mail address: hrzare@yazd.ac.ir (H.R. Zare).



Scheme 1. Structure of (a) [N,N'-bis(salicylaldehyde)-1,2-phenylenediimino cobalt(II)], [Co(II) salophen], and (b) [N,N'-bis(benzoylacetone) ethylenediimino cobalt(II)], [Co(II) bzaen].

N,N'-bis(salicylaldehyde)-1,2-phenylenediimine, Salophen, was synthesized according to the literature [13]. Then, to a stirred solution of $\text{Co}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.249 g, 1 mmol) in methanol (30 mL) under Ar atmosphere an equimolar of N,N'-disalicylidene-1,2-phenylenediamine (0.316 g, 1 mmol) was added. The red solution turned brown immediately upon the formation of [Co(II) salophen] complex. The mixture was stirred at room temperature for about 30 min and then filtered. The powder was filtered off, washed with cold methanol, and dried under a vacuum.

$\text{Co}(\text{OH})_2$ was freshly prepared by adding an NaOH aqueous solution to a solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in water (with a molar ratio of 2:1), filtering the precipitate immediately, and washing it with acetone. It was used for preparation of [Co(II) bzaen] complex. The N,N'-bis(benzoylacetone) ethylenediimine Schiff base ligand, bzaen, as well as the [Co(II) bzaen] complex were synthesized by the method of McCarthy et al. [14]. All the other chemicals were of analytical reagent grades, purchased from Merck and used without any further purification. The purity of CO_2 and Ar gases was 99.995%.

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 (0.0314 cm^2), a Pt wire as a counter electrode, and an Ag/Ag^+ (0.01 M AgNO_3 in 0.1 M TBAP acetonitrile solution) as a reference electrode. All the potentials were measured and reported versus the reference electrode. Controlled potential coulometry (CPC) and constant current coulometry (CCC) were performed using a SAMA 500 electroanalyzer system in an undivided glass cell equipped with a gas inlet and outlet. A graphite rod and an Ag/Ag^+ (0.01 M AgNO_3 in 0.1 M TBAP acetonitrile solution) were used as the cathode and the reference electrode. Also, a platinum plate (ca. 6 cm^2) and a sacrificial Mg were used as counter (anode) electrodes in CPC and CCC, respectively. ^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. Fourier transform infrared (FTIR) spectrum analysis was obtained on an EQUINOX55 spectrometer.

2.2. Coulometry experiments

Controlled potential coulometry (CPC) and constant current coulometry (CCC) were carried out in 50.0 mL DMF containing

0.1 mol L^{-1} TBAP, 3.0 mmol of benzyl bromide (356 μL), and 0.3 mmol of the complexes (0.112 g of the Co(II) salophen and 0.122 g of the Co(II) bzaen complex) as a catalyst in the absence and the presence of CO_2 . Prior to every experiment, the solution was bubbled with Ar gas for 30 min. Upon atmospheric CO_2 pressure, a constant current with a current density of 10 mA cm^{-2} was applied. The results showed the conversion is completed (100%) after passing 2.8 F mol^{-1} of the starting substrate (benzyl bromide) through the cell at room temperature. The electrolyte solution was continuously stirred by a magnetic stirrer during the electrolysis. Also, in the presence of an atmospheric pressure of CO_2 , a constant potential of -1.70 V was applied until 2.5 F mol^{-1} of starting substrate had been passed through the cell. At the end of the electrolysis, the solvent was removed under reduced pressure, and the residue was treated with 20 mL of 0.5 M HCl and then extracted with diethyl ether (Et_2O) ($4 \times 25 \text{ mL}$). After evaporation of the ether, the residue was re-dissolved in 20 mL of 0.5 M NaOH and extracted with Et_2O ($4 \times 15 \text{ mL}$). Finally, the aqueous fractions were acidified with 5.0 M HCl (5 mL) and extracted with Et_2O ($4 \times 15 \text{ mL}$). The ether was again evaporated, and the residue was characterized by FTIR, ^1H , and ^{13}C NMR.

The spectral characteristics of the product were provided as follows (see Figs. S1–S3 of Supplementary Information): 2-phenylacetic acid: ^1H NMR (CDCl_3 , 400 MHz): δ 3.57 (s, 2H, CH_2), 7.19–7.27 (m, 5H, Ar), 7.95 (br, 1 H), ^{13}C NMR (CDCl_3 , 100.6 MHz): δ 58.81, 127.19, 128.60, 129.39, 133.78, 176.17 ppm, IR: 1709 cm^{-1} ($\text{C}=\text{O}$).

3. Computational procedures

The geometries of studied Co complexes were optimized at the B3-LYP level of theory using the LanL2DZ [15] basis set for the Co atom and the 6-31+G(d) basis set for C, O, and N and H atoms. The effective-core-potentials (ECPs) have been used for Co using LanL2DZ basis set. For the determination of charges on different atoms, further Natural Bond Orbital (NBO) calculations have been carried out using larger basis sets of LanL2TZf [16,17], for Co and 6-311+G(d,p) basis sets for C, O and N atoms. Mulliken charges have been calculated at B3LYP level of theory along with 6-31+G(d) basis sets for C, H, N, O and LanL2DZ for Co. All DFT calculations have been executed using Gaussian software [18].

4. Results and discussion

4.1. Electrocatalytic reduction of benzyl halides by the [Co(II) salophen] complex in the absence and the presence of CO_2

Fig. 1, voltammogram a, shows the cyclic voltammogram of the DMF-TBAP solution at the working electrode surface. It shows no redox peaks in the potential range of -1.0 to -2.5 V under Ar bubbling at room temperature. After addition of CO_2 to the above solution, the cathodic current appears slightly at more negative potential of -2.3 V (Fig. 1, voltammogram b). This cathodic current was ascribed to the reduction of CO_2 to an anion radical CO_2^- at the electrode surface [19,20]. Fig. 1, voltammogram c, is related to the solution containing 1.0 mM benzyl bromide. The voltammogram shows an irreversible broad reduction peak that represents an overall 2e process leading to the hydrodehalogenation of the benzyl bromide [21]. It is well known that the one-electron reduction of organic halides ($\text{R}-\text{X}$) leads to the fragmentation of the carbon-halogen σ bond to form the corresponding radical, R^\cdot , and the halide ion, X^- [21]. Since the reduction potential of R^\cdot produced by the cleavage of the bond is generally more positive than that of the starting organic halide, the reduction peak corresponds to a two-electron process leading to the formation of bromide ions, X^- , and a carbanion, R^- [21]. The cyclic voltammogram of the [Co(II) salophen] complex solution, 0.5 mM, (Fig. 1, voltammogram

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