

Original Research

Promising Electrocatalytic Systems 2,5-di-Me-Pyrazine-di-N-Oxide - Cyclohexanol - Single-Walled and Multi-Walled Carbon Nanotubes for the Simultaneous Metal-Free Oxidation of Cyclohexanol at Anode and Release of Hydrogen Evolution at Cathode

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Abstract

Electrocatalytic oxidation of organic compound in the absence of noble metals or their oxides as catalysts and using metal-free electrodes is a "green" electrochemical, inexpensive and attractive process for practical use in electrocatalysis, power sources and sensors. The process accompanied by the elimination of protons, is of interest both for obtaining valuable organic compounds at the anode and for the release of hydrogen evolution at the cathode. In this work, the catalytic oxidation of cyclohexanol in the presence of 2,5-di-Me-pyrazine-di-N-oxide (Pyr₁), as mediator, at glassy carbon (GC) electrode and single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) paper electrodes in 0.1 M Bu₄NClO₄ solution in acetonitrile (MeCN) was studied using cyclic voltammetry (CV) and quantum chemical modeling. It was found that the catalytic efficiency of cyclohexanol



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oxidation at MWCNT and SWCNT paper electrodes is 20 and 32, respectively, which is an order of magnitude higher compared to GC electrode. This effect is explained by quantum chemical modeling and calculation of the energies of non-covalent interactions between the components of the electrocatalytic system in the complexes $C_6H_{11}OH \cdot Bu_4NClO_4$, $MeCN \cdot Bu_4NClO_4$, $Pyr_1 \cdot C_6H_{11}OH$, $C_6H_{11}OH \cdot C_6H_{11}OH$ and $C_6H_{11}OH \cdot MeCN$ in solution, as well as the energies of adsorption of $C_6H_{11}OH$ and the complexes of $Pyr_1 \cdot C_6H_{11}OH$, $C_6H_{11}OH \cdot Bu_4NClO_4$ on the CNT surface using a cluster model describing the surface of conductive carbon nanotubes (10, 10). The high catalytic efficiency of cyclohexanol oxidation at SWCNT and MWCNT paper electrodes indicates the potential of using the studied catalytic systems for simultaneous obtaining valuable organic compounds at the anode and for the release of hydrogen evolution at the cathode as well as in electrocatalysis, power sources, sensors.

Keywords

Electrocatalytic oxidation; cyclic voltammetry; quantum chemical modeling; GC, SWCNT and MWCNT paper electrodes; 2,5-di-Me-pyrazine-di-N-oxide; cyclohexanol

1. Introduction

The search for new energy sources has drawn the attention of researchers to the processes of simultaneous electrooxidation of organic compounds, which occur with the elimination of protons: the production of valuable organic compounds at the anode and the generation of hydrogen at the cathode [1]. The use of carbon nanomaterials as electrode materials is attractive due to their unique physicochemical properties: highly developed surface area, high electrical conductivity, chemical stability, and a wide range of working potentials. Electrochemical oxidation of alcohols (methanol, ethanol, etc.) [2] is used in liquid fuel cells for the simultaneous production of valuable chemical products at the anode and hydrogen at the cathode. The most effective catalysts for the concurrent catalytic oxidation of organic compounds and hydrogen evolution reaction are noble metals (Pt, Ir, Ru, and Pd) or their oxides (IrO_2 and RuO_2), which modify SWCNT and MWCNT electrodes [3-7]. However, the high cost of noble metals or noble metal oxides and their limited availability stimulate a search for non-noble metal or metal-free alternative materials. Carbon nanomaterials doped with heteroatoms (nitrogen, boron, phosphorus, and sulfur) act as metal-free catalysts [8-13] and can be used as catalysts for organic electrooxidation at the anode and hydrogen evolution at the cathode.

In our works, the electrocatalytic oxidation of organic compounds is investigated in the presence of electrochemically generated radical cations of aromatic-di-N-oxides at GC electrode and at SWCNT and MWCNT paper electrodes. In these systems, electrocatalytic oxidation of organic compounds is accompanied by proton elimination and occurs in the absence of precious metals or their oxides as catalysts, on metal-free electrodes. Therefore, these electrocatalytic systems can be promising for simultaneous electrocatalytic organic oxidation at the anode and hydrogen evolution at the cathode.

Oxidation of aromatic di-N-oxides in the absence and presence of organic substrates (alcohols, ethers and cyclohexane) was studied at GC and Pt electrodes in 0.1 M LiClO₄ solutions in acetonitrile [14-20] by the use of cyclic voltammetry, EPR electrolysis, and quantum chemical modeling. The effect of temperature, oxygen, additions of pyridine, water (as a base) and trifluoroacetic acid (CF₃COOH) on the cyclic voltammograms of aromatic di-N-oxides oxidation and the intensity of EPR signals of radical cations was investigated.

It was established [14-20] that the electrochemically generated at GC and Pt electrodes in 0.1 M LiClO₄ solution in MeCN radical cations of aromatic di-N-oxides (the first electrode stage, E₁): phenazine di-N-oxide (PhenDNO), 2,3,5,6-tetra-Me-pyrazine di-N-oxide (Pyr₂), 2,5-di-Me-pyrazine di-N-oxide (Pyr₁) and pyrazine di-N-oxide (Pyr₀) contain active oxygen in their structure, which activates the C-H bond of substrates: alcohols, ethers and cyclohexane. Activation occurs in the process of the electrophilic addition of oxygen of the radical cation of aromatic di-N-oxide to the C-H bond of the substrate (the first chemical stage, C₁). The reaction is accompanied by the elimination of a proton and the formation of a radical intermediate - a complex of a radical-cation with a substrate with the -N-O-C- structure. The compounds of this structure and methods for their preparation are known [21-27]. Due to the high reactivity of the radical cation, registration of radical intermediate was possible only in the process of EPR electrolysis [16] at the oxidation of phenazine-di-N-oxide in MeOH and its deuterated derivatives when using alcohols as substrates and solvents simultaneously and at temperatures close to the freezing temperatures of alcohols. The registration of the same radical intermediate in CH₃OH and CH₃OD alcohols indicated participation of the CH₃ group of alcohol in the formation of the intermediate. The radical intermediate formed in stage (C₁) is oxidized to a cation in the second electrode stage (E₂). In the subsequent chemical reaction of cation with a base or nucleophile, accompanied by proton elimination (the second chemical stage, C₂), the cation decomposes with the regeneration of the original aromatic di-N-oxide and the product of two-electron oxidation of the substrate. The regenerated aromatic di-N-oxide is immediately oxidized to the radical cation and the cycle repeats again. Based on cyclic voltammetry data, electron paramagnetic resonance (EPR) electrolysis and quantum chemical modeling [14-20], an E₁C₁E₂C₂ mechanism for the total two-electron electrocatalytic oxidation of the substrate in a complex with di-N-oxide radical cation with the catalysis at the second electrode stage was proposed.

Electrocatalytic oxidation of organic compounds is accompanied by the elimination of protons (in the stage of activation of the C-H bond, stage C₁, and in the stage of regeneration of the initial di-N-oxide, stage C₂). Thus, the total two-electron electrocatalytic oxidation of organic compounds is accompanied by the elimination of two protons. An increase in the catalytic efficiency of the oxidation of organic compounds leads to a directly proportional increase in the concentration of the formed protons and, consequently, the concentration of hydrogen generated at the cathode. This fact indicates the possibility of simultaneously electrocatalytically oxidizing an organic compound at the anode and generating hydrogen at the cathode.

It should be noted that with an increase in the oxidation potential of aromatic di-N-oxide, the catalytic efficiency of the organic substrate oxidation increases. The catalytic efficiency is the ratio of the catalytic current for di-N-oxide oxidation recorded in the presence of an organic substrate to the diffusion current for di-N-oxide oxidation recorded in the absence of a substrate, or ferrocene, used as a reference. However, with the increase in the oxidation potential of the di-N-oxide, a competing reaction of the di-N-oxide radical cation with acetonitrile (solvent) appears.

The oxidation of PhenDNO in 0.1 M LiClO₄ at GC or Pt electrodes ($E_{ox} = 1.28$ V, [16]) to the radical cation is a one-electron, reversible, diffusion-controlled process. Oxidation of Pyr₂ ($E_{ox} = 1.48$ V, [18]) is a one-electron, diffusion, quasi-reversible process. Oxidation of Pyr₁ ($E_{ox} = 1.56$ V, [18]) and Pyr₀ ($E_{ox} = 1.62$ V, [17]) are one-electron, irreversible, diffusion-controlled processes since their oxidation is accompanied by the irreversible chemical reaction with the solvent following the electrode process. The rate constant of the chemical reaction was determined by the method of Nicholson and Shain [28, 29] and Galus [30] and was found to be 1.6 s⁻¹ for Pyr₂, 2 s⁻¹ for Pyr₁ and 8 s⁻¹ for Pyr₀, [18]. The one-electron process of di-N-oxides oxidation is confirmed by recording the EPR spectra of the corresponding radical cations during EPR electrolysis at controlled potentials only when the temperature drops to -45°C (a temperature close to the freezing point of the solvent, MeCN), which is explained by the high reactivity of radical cations [18]. The intensity of the EPR spectra of radical cations of aromatic di-N-oxides reached a maximum at a potential of 1.6 V. It did not change with an increase in the electrolysis potential to 2.4 V. Consequently, further oxidation of radical cations to dications does not occur in this potential range.

It was found [31-38] that the catalytic efficiency of oxidation of organic substrates (cyclohexanol, isopropyl alcohol, methanol, tertiary butyl alcohol and cyclohexane) in the presence of aromatic di-N-oxides at SWCNT or MWCNT paper electrodes increases several times compared with the GC electrode. A special feature of the studied electrocatalytic systems is the identity of the structures of the aromatic di-N-oxides and the CNT electrodes. It was proposed [39] to consider the aromatic molecules/CNT systems as two interacting π -systems, since the adsorption of the aromatic molecules on the CNT surface is due to the π - π interaction of the π -orbitals of the benzene ring and CNT.

Quantum chemical modeling and calculation of the adsorption energy of Pyr₁ and Fc (ferrocene, as reference) [40], as well as components of the catalytic systems and their complexes (Pyr₁-MeOH-CNT) [35, 36], (Pyr₁-tert-BuOH-CNT) [37] and (Pyr₁-C₆H₁₂-CNT) [38] on CNT surface allowed to explain the effect of increasing the catalytic efficiency at using CNTs electrodes and to propose the oxidation mechanism of MeOH, tert-BuOH and C₆H₁₂ (cyclohexan) at CNTs electrodes.

In this work, the features of electrocatalytic oxidation of cyclohexanol in the presence of mediator Pyr₁ at SWCNT and MWCNT paper electrodes in comparison with the GC electrode in 0.1 M Bu₄NClO₄ solution in MeCN were studied using cyclic voltammetry and quantum chemical modeling. The influence of Pyr₁ and cyclohexanol concentrations, the presence of acid (CH₃COOH), and water as a base on the catalytic process was studied. The energies of non-covalent interactions between the components of the electrocatalytic system in the complexes C₆H₁₁OH*Bu₄NClO₄, Pyr₁*C₆H₁₁OH, C₆H₁₁OH*C₆H₁₁OH and C₆H₁₁OH*MeCN in solution were calculated using quantum-chemical modeling. The adsorption energies of C₆H₁₁OH and complexes of C₆H₁₁OH*Bu₄NClO₄ and Pyr₁*C₆H₁₁OH on the CNT surface were determined using a cluster model proposed in [40] and describing the surface of conductive carbon nanotubes (10, 10). During the study, factors leading to an increase in the catalytic efficiency of the process were identified and a mechanism for the electrocatalytic oxidation of cyclohexanol in the presence of Pyr₁ on CNT electrodes was proposed. The obtained data open up new possibilities for using these new carbon-based electrode materials. This knowledge is useful for the use of aromatic di-N-oxide - cyclohexanol - CNTs electrocatalytic systems for simultaneous oxidation of cyclohexanol at the anode and generation of hydrogen at the cathode ("green hydrogen energy"), as well as for electrocatalysis, power sources, and sensors.

2. Materials and Methods

Materials, experimental and quantum-chemical modeling techniques are described in detail in our previous works [35, 40]. The CVs were recorded at GC, SWCNT and MWCNT paper electrodes using a potentiostat–galvanostat PX-40 (Moscow, Russia). A three-electrode cell was used for electrochemical measurements. Before the experiment, the GC electrode was polished with micron sandpaper. Then, the GC electrode, SWCNT and MWCNT paper electrodes were washed with acetone and tridistilled water and dried. The visible surface of GC was 0.181 cm². A platinum plate served as the counter electrode. The reference electrode was a silver wire placed in a separate vessel filled with 0.1 M Bu₄NClO₄ solution in acetonitrile and separated from the main part of the cell by a porous filter. The accuracy of potential recording was ±0.01 V. The solution of 0.1 M Bu₄NClO₄ in acetonitrile was used as a background solution in all experiments. Note that before every new experiment, fresh SWCNT and MWCNT paper electrodes were made from the initial material.

Before the experiments, oxygen dissolved in the solution was removed by bubbling argon (high purity grade) through the cell. During experiments, the argon flow over the solution prevents the penetration of oxygen into the solution. Before recording the CV in 0.1 M Bu₄NClO₄ solution in acetonitrile, the electrodes were polarized twice for 10 s at 1.0 and 1.5 V, and then CVs were recorded in the potential range of 1.0 to 2.2 V. Before recording each CV in the investigation solution, the electrodes were polarized for 40 s at 1.0 V.

Electrodes from carbon nanopaper were obtained as described in [41]. The size of working nanopaper electrodes was 2 × 4 mm. MWCNT paper (>95% purity) was produced by “NanoLab’s” firm (USA) as a black sheet-like material with a thickness of 0.1 mm. According to our data of scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) [34], nanopaper contains multi-walled carbon nanotubes with a diameter of ~20 nm and length of ~2 μm. SWCNT paper (>95% purity) was purchased from “Advanced Chemical Supplier Material, LLC’s” firm (USA). Nanopaper with a thickness of 0.01-0.02 mm contains SWCNT with a diameter of 0.8-1.6 nm and a length of ~1-3 μm, and less than 0.5% metals. Acetonitrile and cyclohexanol of HPLC grade were used. Bu₄NClO₄ was of electrochemical grade (>99%, Chemica Fluka’s firm, Switzerland). The experimental procedure of the Pyr₁ synthesis was described in [42].

2.1 Computational Design Procedure

In this paper, a simulation of experimentally observed oxidation of Pyr₁ at bundles of conducting CNTs with diameters between 0.8 and 1.6 nm was carried out. Therefore, conductive CNTs (10, 10) with diameters of 1.41 nm were used for the simulation of a nanotube. The geometry parameters of this CNT were fully optimized in the frame of the PBC (periodic boundary conditions) approach with the PBE hybrid density functional [43-45] and the projector augmented wave (PAW) [46] basis set with energy limit 400 eV. For calculations, the Vienna Ab initio Simulation Package (VASP) [47-50] was used.

For the simulation of the CNT surface, the C₅₄H₁₈ model cluster with coordinates of C atoms taken from the calculated CNT (PBC) was used. To preserve the shape of the CNT surface, these coordinates were fixed in the process of optimizing the geometry of the combined systems. Dangling bonds in the model cluster were terminated by H atoms. For combined systems (including model cluster simulating CNT surface and adsorbed molecules), only the optimized

coordinates of adsorbate molecules were used. For the modeling of the combined systems, the ω B97XD [43-45] hybrid density functional was used, adjusted for the simulation of dispersion interactions. A moderate 6-31G(d,p) basis set was used for geometry optimization. The energy values for the obtained structures were refined with more complete 6-311G(d,p) and aug-cc-pVTZ basis sets with the same ω B97XD density functional and with account of BSSE (basis set superposition error) effect. It is worth noting that the energy values obtained with the used basis sets differ by 2-4 kcal/mol, but the trends in the series are identical. The interaction energies of adsorbed molecules with the CNT surface (E_b) were determined as follows: $E_b = E_{A*B} - (E_A + E_B)$, where E_{A*B} is the energy of the combined A*B system, E_A and E_B are the energies of the isolated fragments. Negative value of E_b corresponds to the attraction of the fragments. At this stage, the GAUSSIAN 09 software package [51] was used.

The influence of solvent media (acetonitrile) was modeled in the frame work of IEFPCM (Integral Equation Formalism with Polarizable Continuum Model) approach by means of SCRF (Self-Consistent Reaction Field) method. The appropriate data are designated by the index "s". The solvent effect does not change geometry and relative energies essentially (~1-3 kcal/mol) and does not lead to qualitative variations of calculated results.

3. Results and Discussion

3.1 Non-Covalent Binding Energy in Complexes

Energies of non-covalent interactions (E_b , kcal/mol) in complexes obtained at different levels of calculation are shown in Figure 1. The values of binding energy in the complexes are given in the following sequence: a) in solution: **1.** $C_6H_{11}OH \cdot Bu_4NClO_4$ > **2.** $Pyr_1 \cdot Bu_4NClO_4$ [36] > **3.** $MeCN \cdot Bu_4NClO_4$ > **4.** $Pyr_1 \cdot Pyr_1$ [36] > **5.** $Pyr_1 \cdot C_6H_{11}OH$ > **6.** $C_6H_{11}OH \cdot C_6H_{11}OH$ > **7.** $Pyr_1 \cdot MeCN$ [36] > **8.** $MeCN \cdot MeCN$ [36] > **9.** $C_6H_{11}OH \cdot MeCN$; b) the adsorption energy on the CNT surface: **10.** $Pyr_1 \cdot Bu_4NClO_4 \cdot CNT$ [37] > **11.** $Bu_4NClO_4 \cdot CNT$ [36] > **12.** $Pyr_1 \cdot C_6H_{11}OH \cdot CNT$ > **13.** $C_6H_{11}OH \cdot Bu_4NClO_4 \cdot CNT$ > **14.** $Pyr_1 \cdot CNT$ [40] > **15.** $Pyr_1 \cdot MeCN \cdot CNT$ [37] > **16.** $C_6H_{11}OH \cdot CNT$ > **17.** $MeCN \cdot CNT$ [40].

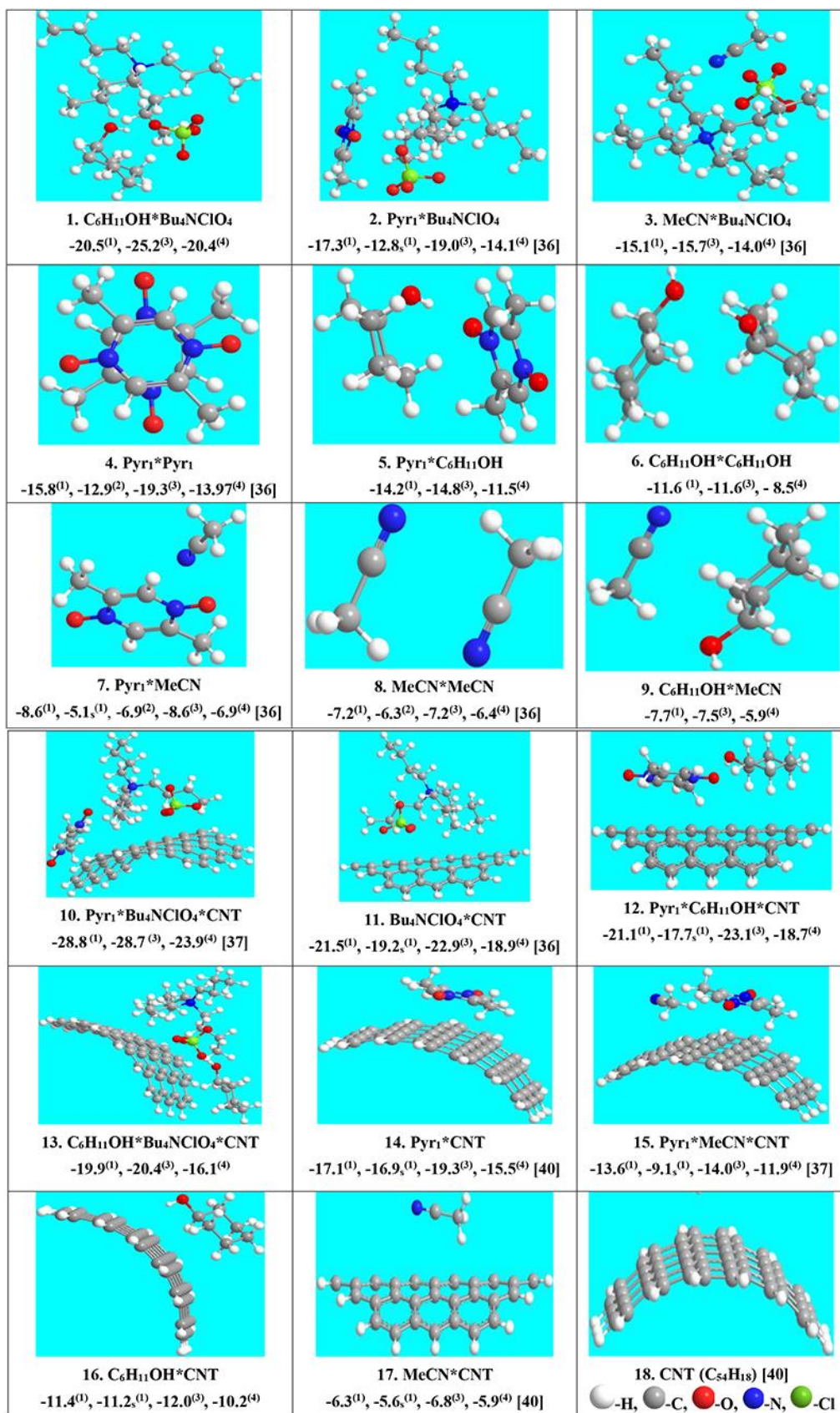


Figure 1 Structure and binding energies (E_b , kcal/mol) in complexes. The SCF levels of calculation are given: ⁽¹⁾wB97XD//6-31G(d,p), ⁽²⁾wB97XD/aug-cc-pVTZ, ⁽³⁾wB97XD//6-31G(d,p)//6-311G(d,p), ⁽⁴⁾wB97XD/6-31G(d,p)//6-311G(d,p)(BSSE), s - solvent accounting by SCRF method.

3.2 Oxidation of Pyr₁ at GC, SWCNT and MWCNT Paper Electrodes in MeCN

3.2.1 In the Absence of Cyclohexanol

Oxidation of Pyr₁ ($E_{ox} = 1.56$ V) was studied at GC electrode [14-20, 40], SWCNT and MWCNT paper electrodes [40] in background solution using methods of cyclic voltammetry, EPR electrolysis, and quantum chemical modeling. It has been established that the oxidation of Pyr₁ at the GC electrode is a one-electron, irreversible and diffusion-controlled process. The irreversibility of the electrode process is due to the subsequent irreversible chemical reaction of the radical cation of Pyr₁ with the solvent (watch Introduction). Cyclic voltammograms of oxidation of 1 mM Pyr₁ obtained in this work at GC electrode, SWCNT and MWCNT paper electrodes in background solution at different scan rates are shown in Figure 2.

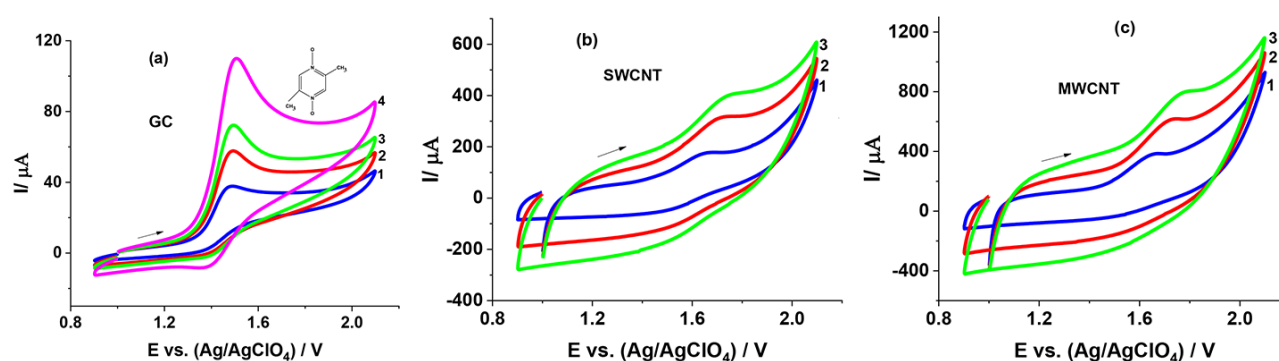


Figure 2 CVs of 1 mM Pyr₁ in background solution: (a) at GC electrode, (b) at SWCNT and (c) at MWCNT paper electrodes at scan rates (1) 20, (2) 50, (3) 80, (4) 200 mV/s.

At SWCNT and MWCNT paper electrodes, the oxidation of Pyr₁ is irreversible and not controlled by diffusion [40]. In contrast to the GC electrode, the oxidation currents of Pyr₁ at the SWCNT and MWCNT paper electrodes are several times higher than the diffusion current of Fc oxidation (as reference). These data are consistent with the data of the work [40].

It was shown [40] that the oxidation of Fc ($E_{ox} = 0.28$ V) at GC electrode, SWCNT, and MWCNT paper electrodes (Figure 3) is a one-electron, reversible, and diffusion-controlled process, so Fc can be used as a reference in studying electrode processes at these electrodes. This is evidenced by the following: the difference between the anode and cathode peaks is 60 mV, the values of the currents of the anode and cathode peaks are equal to each other, the currents of the anode and cathode peaks increase in direct proportion to the square root of the scan rate, and are directly proportional to the concentration of Fc.

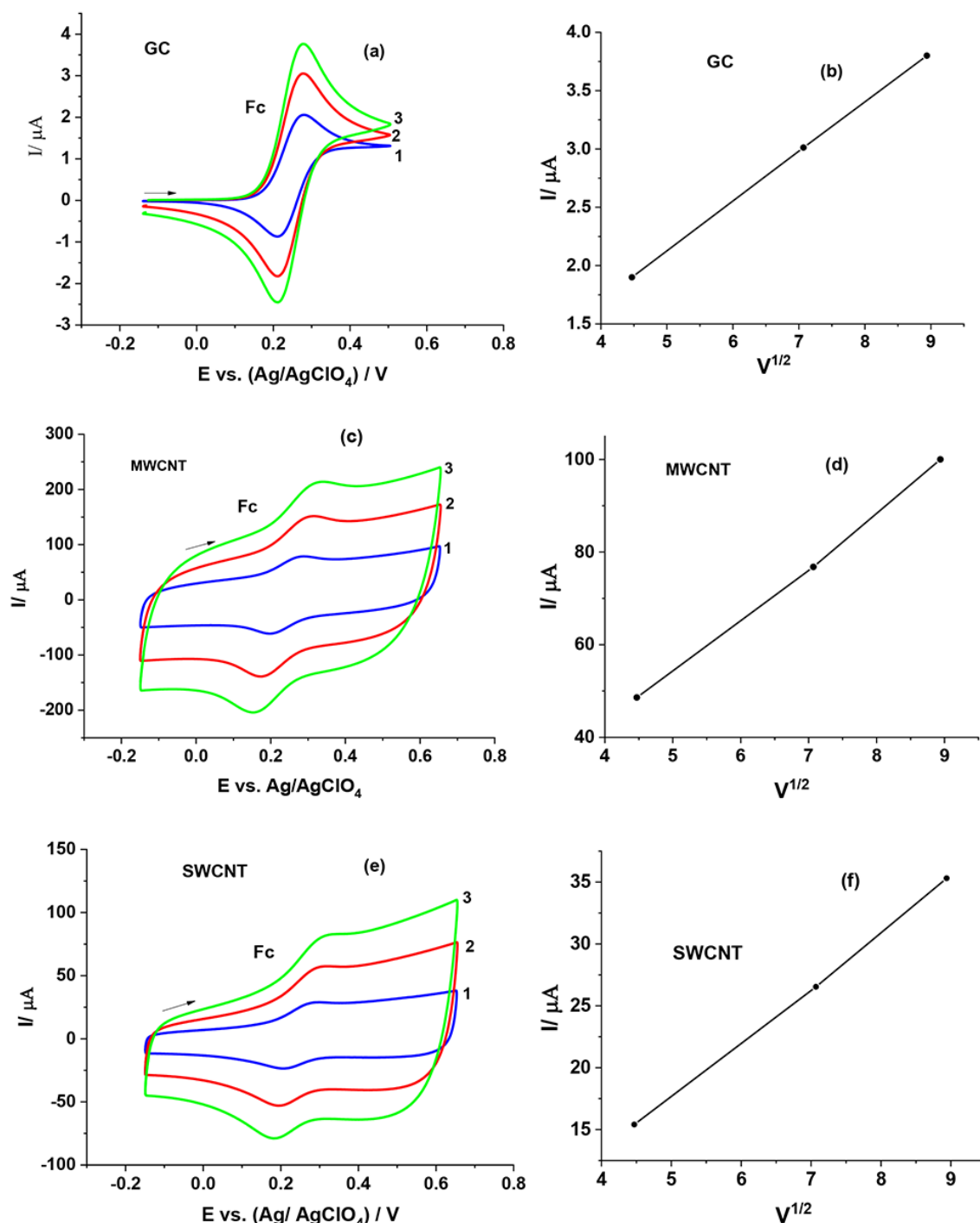


Figure 3 CVs in the background solution from [40]: at (a) GC and (c) MWCNT, (e) SWCNT paper electrodes in the presence of 1 mM Fc at scan rates of (1) 20, (2) 50, (3) 80 mV/s ; dependence of the anode peak current on the square root of scan rates at (b) GC and (d) MWCNT, (f) SWCNT paper electrodes.

Quantum chemical modeling and calculation of the adsorption energy of Pyr_1 and Fc on the CNT surface [40] established that the adsorption energy of Pyr_1 , in contrast to Fc, exceeds the adsorption energy of solvent molecules displaced from the CNT surface, as a result of Pyr_1 adsorption, its concentration on the CNT surface increases and, as a consequence, the current of Pyr_1 oxidation increases. Oxidation of 1 mM Pyr_1 at SWCNT and MWCNT paper electrodes is

recorded at potentials 200 mV higher than at the GC electrode. This is explained [40] by the need to overcome the adsorption energy of Pyr₁ molecules on the CNT surface.

It should be noted that the linear dependence of the oxidation currents of Pyr₁ on CNT electrodes on the scan rate, which is typical for adsorption currents, is not observed. This is explained by the fact that CNT electrodes have a highly developed surface and, therefore, exhibit high capacitive currents, that increase, just like adsorption currents, in direct proportion to the scan rate. We have found that the scan rate on CNT electrodes can be increased only up to 80 mV/s, since a further increase leads to the predominance of capacitive currents over oxidation currents of the di-N-oxide.

3.2.2 In the Presence of Cyclohexanol

CV curves registered at the GC electrode in the background solution in the absence of Pyr₁ with the addition of 0.05-1.0 M cyclohexanol (Figure 4a) confirm that oxidation of cyclohexanol in the absence of Pyr₁ is not observed in the potential range from 1.0 to 2.1 V.

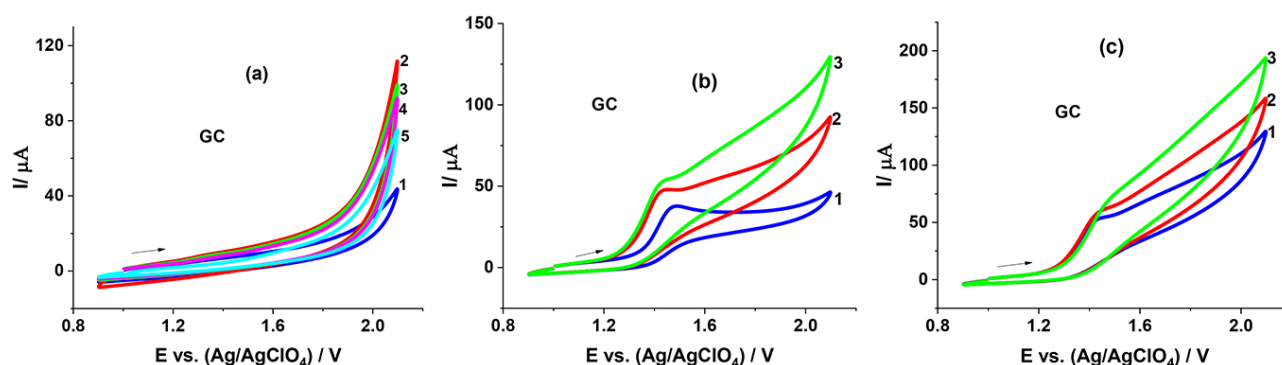


Figure 4 CVs in background solution at GC electrode at a scan rate of 20 mV/s in the presence of cyclohexanol: (a) (1) 0, (2) 0.05, (3) 0.1, (4) 0.5, (5) 1.0 M; (b, c) 1 mM Pyr₁ and cyclohexanol: (b) (1) 0, (2) 0.01, (3) 0.05; (c) (1) 0.05, (2) 0.1, (3) 0.5 M.

When 0.01-0.05 M cyclohexanol was added to a solution containing 1 mM Pyr₁, the cathode wave of reduction of the Pyr₁ radical cation to Pyr₁ at the GC electrode, recorded during the reverse potential scan from 2.1 V to 0.9 V, disappeared (Figures 4b, c), indicating the interaction of the Pyr₁ radical cation with cyclohexanol. Simultaneously, a second anodic wave appears in the potential range from 1.55 V to 1.9 V, the current peak of Pyr₁ oxidation of the first wave increases, and its potential shifts by 35 mV toward lower positive values (Figure 4b). With an increase in the concentration of cyclohexanol from 0.01 to 0.5 M, the current of the second anode wave increases and at a concentration of 0.5 M cyclohexanol, the first and second anode waves merge (Figure 4c). In the presence of 1 mM Pyr₁ and 0.01 M cyclohexanol, the start of the second anodic wave at the GC electrode shifts to the region of higher positive potential with an increase in the scan rate from 20 to 200 mV/s (Figure 5).

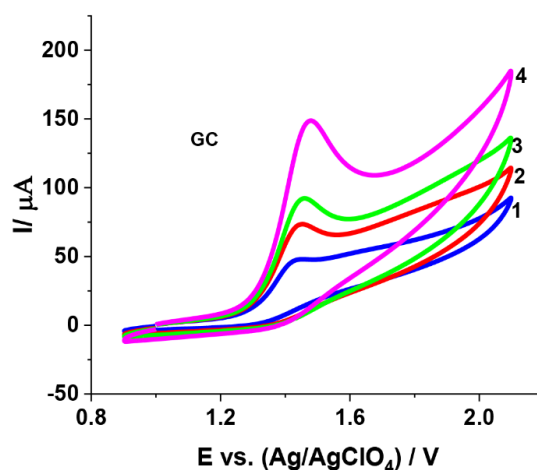


Figure 5 CVs in background solution at GC electrode in the presence: (a) 1 mM Pyr₁ and 0.01 M cyclohexanol at a scan rate: (1) 20, (2) 50, (3) 80, (4) 200 mV/s.

Figure 6 shows a comparison of cyclic voltammograms obtained in a background solution at a GC electrode in the presence of 1 mM Pyr₁ and in the absence and presence of 0.5 M cyclohexanol with a change in scan rate from 20 to 200 mV/s. From the comparison, it follows that with an increase in the scan rate, the start of the catalytic wave shifts to the region of higher anodic potentials, and at 200 mV/s, its beginning coincides with the wave of 1 mM Pyr₁ oxidation, recorded in the absence of cyclohexanol.

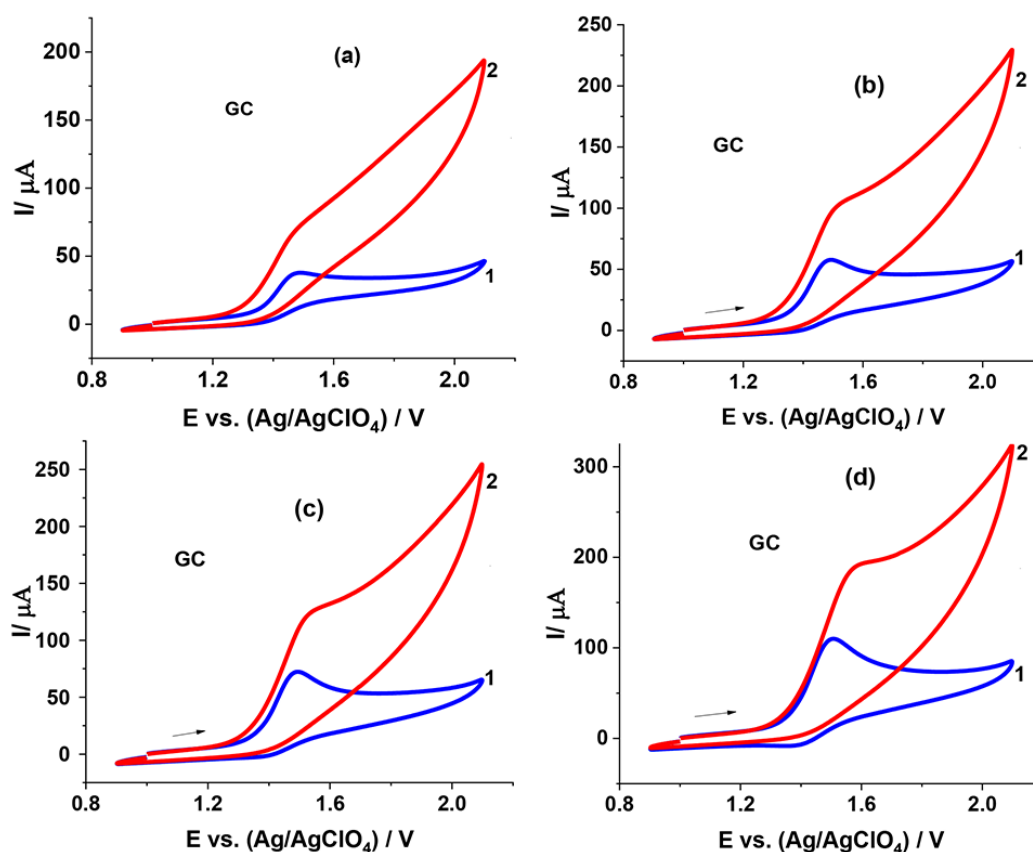


Figure 6 CVs in background solution at GC electrode in the presence: (1) 1 mM Pyr₁, (2) 1 mM Pyr₁ and 0.5 M cyclohexanol at a scan rate: (a) 20, (b) 50, (c) 80, (d) 200 mV/s.

At the GC electrode, the catalytic efficiency of the process (the ratio of peak currents in the presence of 1 mM Pyr₁ and 0.5 M cyclohexanol to the diffusion current of Pyr₁ oxidation in the absence of cyclohexanol) is 2. Note that the catalytic currents increase in direct proportion to the increase in the Pyr₁ concentration from 0.5 to 1 M (Figure 7).

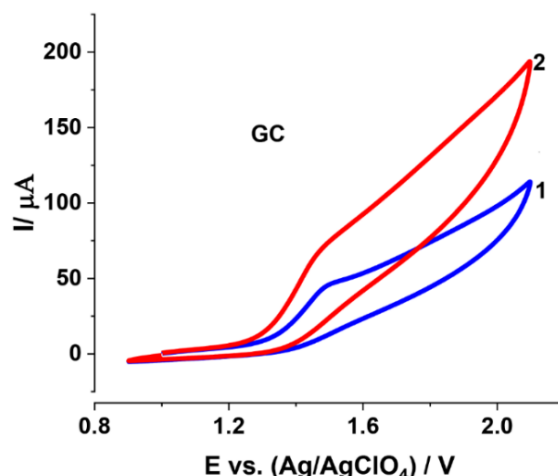


Figure 7 CVs in background solution at GC electrode at a scan rate 20 mV/s in the presence of 0.5 M cyclohexanol and Pyr₁: (1) 0.5, (2) 1 mM.

According to the previously proposed mechanism [14-20] (see Introduction), electrocatalytic oxidation of the organic substrate is accompanied by proton elimination. Therefore, the presence of water as a base will accelerate the catalytic process, while the presence of an acid will inhibit it. Indeed, upon the addition of 1-2 M water to the background solution containing 0.5 mM Pyr₁ and 0.5 M cyclohexanol, anodic currents at the GC electrode increased (Figure 8a). The ratio of anodic currents in the presence of 2 M H₂O to the currents recorded in the absence of water is 5.5. When 1 and 2 M CH₃COOH is added to a background solution containing 1 M Pyr₁ and 0.5 M cyclohexanol, the catalytic current on the GC electrode decreases and shifts by 200 mV to the region of higher positive potential values (Figure 8b). The obtained data confirm that the catalytic process of cyclohexanol oxidation in the presence of Pyr₁ is accompanied by proton elimination.

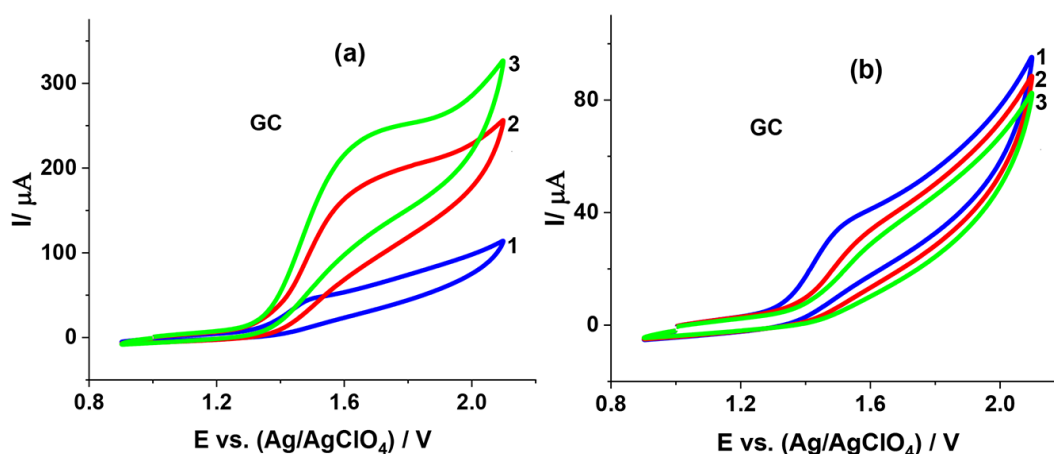


Figure 8 CVs in background solution at GC electrode at a scan rate 20 mV/s in the presence: (a) 0.5 mM Pyr₁ and 0.5 M cyclohexanol and H₂O: (1) 0, (2) 1, (3) 2 M; (b) 1.0 mM Pyr₁ and 0.5 M cyclohexanol and CH₃COOH: (1) 0, (2) 1.0, (3) 2.0 M.

It should be noted that the oxidation mechanism of di-N-oxides in the absence of an organic substrate at GC and Pt electrodes in 0.1 M LiClO₄ in MeCN was investigated in [18] using cyclic voltammetry, EPR electrolysis and quantum chemical modeling methods. The effects of temperature, oxygen, additions of pyridine, water (as a base) and trifluoroacetic acid (CF₃COOH) on the cyclic voltammograms of aromatic di-N-oxides oxidation and the intensity of EPR signals of radical cations were investigated. It was found that upon adding H₂O up to 1 M, the oxidation peak current of 1 mM di-N-oxides increases twofold. The same increase in the anodic peak current was achieved in the presence of 1 mM pyridine, i.e., at a concentration three orders of magnitude lower than that of water. The obtained data indicated that the interaction of the radical cation with acetonitrile is accompanied by proton elimination. Based on the experimental data and quantum chemical modeling of the reaction of the radical cation di-N-oxides with MeCN obtained in [18], it was concluded that the oxidation of aromatic di-N-oxides in MeCN is realized by the E₁C₁E₂C₂ mechanism of total two-electron oxidation of organic substance proposed in [14-17] in a complex with di-N-oxide radical cation.

At SWCNT and MWCNT paper electrodes in the absence of Pyr₁, oxidation of cyclohexanol when its concentration changes from 0.05 to 1 M in the background solution is not registered in the potential range from 1.0 to 2.1 V (Figures 9a, b). When 0.05-0.5 M cyclohexanol was added to background solutions containing 1 mM Pyr₁, the anode currents at the SWCNT and MWCNT paper electrodes increased several fold, and the potential of the current rise shifted towards lower positive values (Figures 9c, d). Since cyclohexanol is both a substrate and a nucleophile, increasing its concentration increases the rate of the oxidation process, which is accompanied by proton elimination, and the potential shifts to lower positive values, as recorded on the CV.

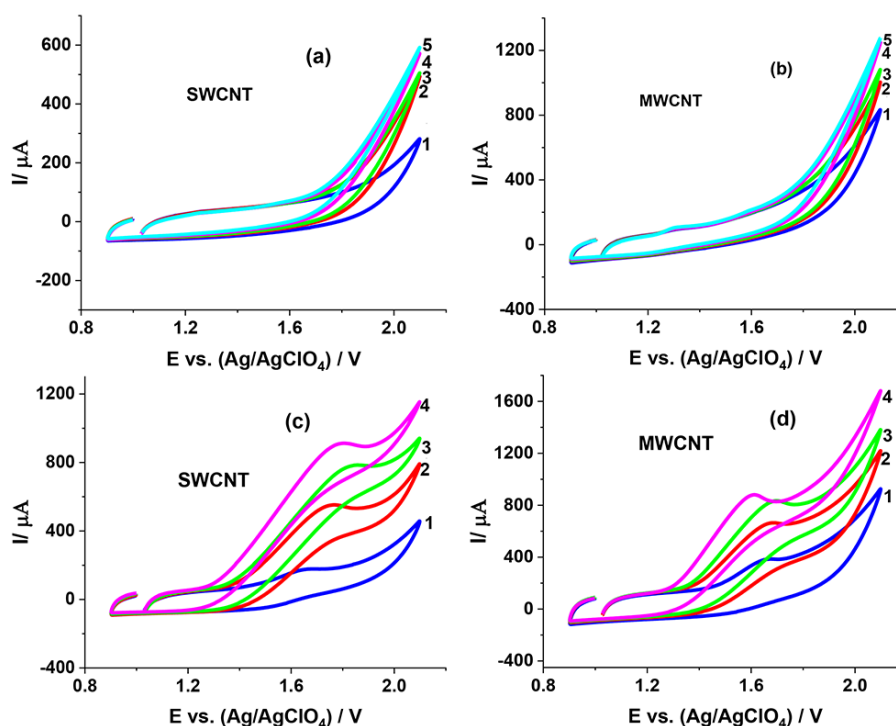


Figure 9 CVs in background solution at a scan rate of 20 mV/s in the presence of cyclohexanol: (1) 0, (2) 0.05, (3) 0.1, (4) 0.5, (5) 1.0 M (a) SWCNT and (b) MWCNT paper electrodes; in the presence 1 mM Pyr₁ and cyclohexanol: (1) 0, (2) 0.05, (3) 0.1, (4) 0.5 M (c) SWCNT and (d) MWCNT paper electrodes.

The catalytic efficiency of the processes α (the ratio of the catalytic current of oxidation of 1 mM Pyr₁ in the presence of 0.5 M cyclohexanol to the diffusion current of 1 mM Fc oxidation) at SWCNT and MWCNT paper electrodes is 32 and 20, respectively (Figures 10a, b). The catalytic currents are directly proportional to the concentration of Pyr₁ (Figures 10c, d) and their dependence on the scan rate is presented in Figures 10e, f.

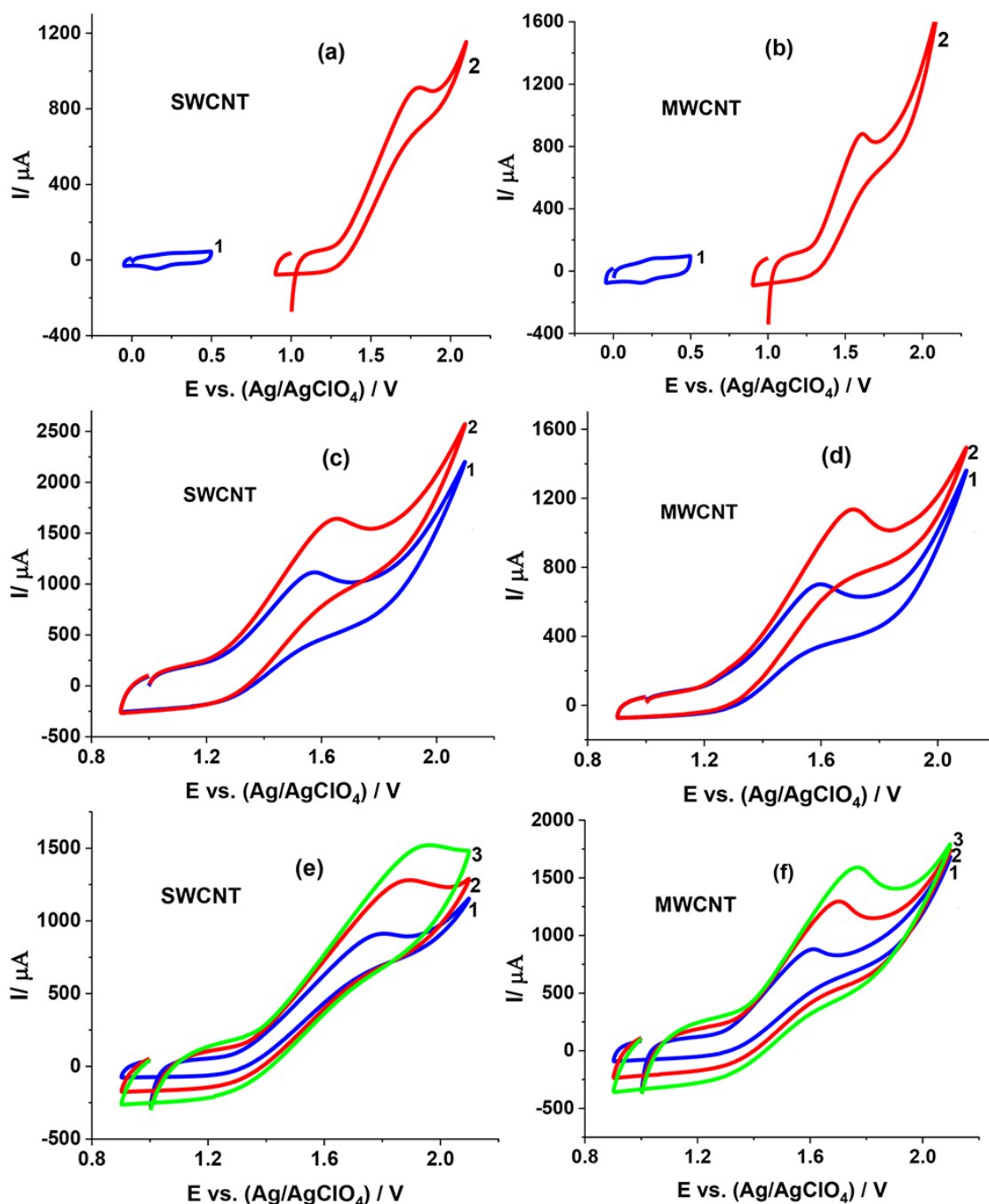


Figure 10 CVs in background solution at a scan rate of 20 mV/s: in the presence (1) 1 mM Fc, (2) 1 mM Pyr₁ and 0.5 M cyclohexanol (a) SWCNT and (b) MWCNT paper electrodes; in the presence of 0.5 M cyclohexanol and Pyr₁: (1) 0.5 mM, (2) 1 mM (c) SWCNT and (d) MWCNT paper electrodes; in the presence of 1 mM Pyr₁ and 0.5 M cyclohexanol at a scan rate: (1) 20, (2) 50, (3) 80 mV/s (e) SWCNT and (f) MWCNT paper electrodes.

With the addition of 1 M H₂O in the background solution containing 0.5 M Pyr₁ and 0.5 M cyclohexanol, the catalytic currents at SWCNT and MWCNT paper electrodes increased, and their potentials became less positive (Figures 11a, b). It should be noted that the influence of H₂O on the catalytic process occurring at SWCNT and MWCNT paper electrodes is expressed less strongly than on the GC electrode. This is explained, according to [35], by the fact that the adsorption energy of water on CNT electrodes (-3 kcal/mol) is significantly lower than the adsorption energy of MeCN solvent (-5.9 kcal/mol) and is insufficient to displace solvent molecules from the surface of CNTs.

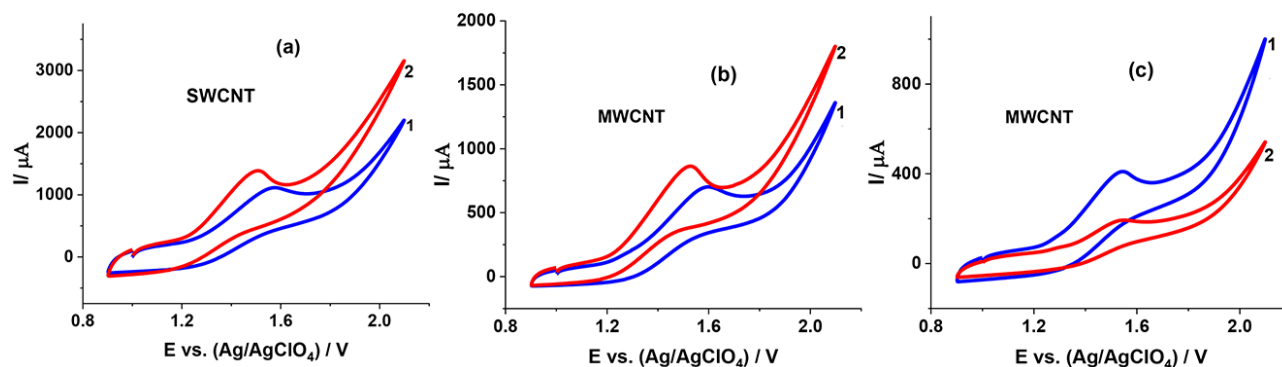


Figure 11 CVs in background solution at a scan rate 20 mV/s: in the presence 0.5 mM Pyr₁ and 0.5 M cyclohexanol and H₂O: (1) 0, (2) 1.0 M; (a) SWCNT and (b) MWCNT paper electrode; in the presence 1.0 mM Pyr₁ and 0.5 M cyclohexanol and CH₃COOH: (c) (1) 0, (2) 1.0 M at MWCNT paper electrode.

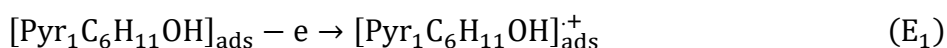
Catalytic current recorded at MWCNT paper electrode in the presence of 1 mM Pyr₁ and 0.5 M cyclohexanol decreases by 2.3 times upon the addition of 1 M CH₃COOH. The difference in the inhibitory effect on GC and MWCNT electrodes is explained by quantum chemical modeling and the calculation of the adsorption energy of CH₃COOH on the CNT electrode [35]. According to [35], the adsorption energy of CH₃COOH (-6.3 kcal/mol) is sufficient to displace MeCN solvent from the CNT surface. At the adsorption of CH₃COOH the acid concentration on CNT increases and the inhibitory effect is stronger compared with the GC electrode. The influence of water (as a base) and acid on the catalytic process indicates that the catalytic process at CNT electrode surfaces is accompanied by proton elimination.

From quantum chemical calculation of the energy of non-covalent interactions between the components of the catalytic system Pyr₁ - C₆H₁₁OH in background solution and the adsorption energy of components on CNTs (Figure 1) follows. The studied solutions contain C₆H₁₁OH*Bu₄NClO₄, Pyr₁*Bu₄NClO₄ and MeCN*Bu₄NClO₄ complexes with non-covalent interaction energies of -20.4⁽⁴⁾, -14.1⁽⁴⁾ and -14.0⁽⁴⁾ kcal/mol, respectively. On the uncharged surface of CNTs electrodes, Pyr₁*Bu₄NClO₄*CNT, Bu₄NClO₄*CNT and Pyr₁*C₆H₁₁OH*CNT complexes will be present, since their adsorption energies are equal to -23.9⁽⁴⁾, -18.9⁽⁴⁾ and -18.7⁽⁴⁾ kcal/mol, respectively, and exceed the adsorption energies of other components of the catalytic system. On the positively charged surface of CNT electrodes, the Pyr₁*Bu₄NClO₄*CNT and Bu₄NClO₄*CNT complexes will be absent as the adsorption of Bu₄N⁺ cations is impossible, ClO₄⁻ anions will be present. The complex Pyr₁*C₆H₁₁OH*CNT will be present and participate in the catalytic process, since its adsorption energy equal -18.7⁽⁴⁾ kcal/mol exceeds the adsorption energies of complexes Pyr₁*MeCN*CNT (-

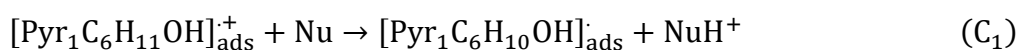
11.9⁽⁴⁾ kcal/mol) and C₆H₁₁OH**CNT* (-10.2⁽⁴⁾ kcal/mol) (Figure 1). The adsorption energy of C₆H₁₁OH**CNT* significantly exceeds the adsorption energy of MeCN**CNT* (-5.9⁽⁴⁾ kcal/mol). This suggests that the concentration of cyclohexanol on the *CNT* surface will be higher than the concentration of MeCN, and therefore, the contribution of the competing reaction of the Pyr₁ radical cation with MeCN will be insignificant.

Based on quantum-chemical modeling and the obtained experimental data, the following mechanism for Pyr₁ oxidation in the presence of cyclohexanol at SWCNT and MWCNT paper electrodes can be proposed.

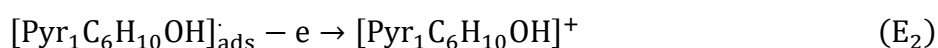
E₁ - First Electrode Stage. [Pyr₁C₆H₁₁OH]_{ads} complex adsorbed on the *CNT* surface is oxidized to the radical cation. This process is irreversible and not controlled by diffusion.



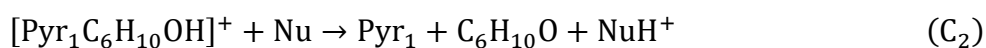
C₁ - First Chemical Stage. In the chemical stage, the [Pyr₁C₆H₁₁OH]_{ads}⁺ radical cation adsorbed on the *CNT* surface reacts with a base or nucleophile. The process involves proton elimination and the formation of a radical intermediate adsorbed on the *CNT* surface.



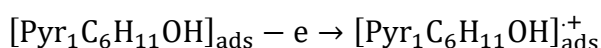
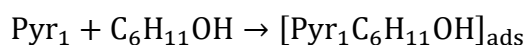
E₂ - Second Electrode Stage. The radical intermediate adsorbed on the *CNT* surface is oxidized to the cation.



C₂ - Second Chemical Stage. In the second chemical stage, the cation reacts with a nucleophile or base (an admixture of water in the solution) with the elimination of a proton and the formation of the initial aromatic di-N-oxide and cyclohexanone, a product of the two-electron oxidation of cyclohexanol.



The regenerated aromatic di-N-oxide forms a complex with cyclohexanol [Pyr₁C₆H₁₁OH]_{ads} which is further oxidized to a radical cation [Pyr₁C₆H₁₁OH]_{ads}⁺. The cycle is repeated, and the catalytic current of the total two-electron oxidation of cyclohexanol is recorded.



It should be noted that cyclohexanol and cyclohexanone were detected in the products of electrolysis carried out at a controlled potential (+1.8 V) on a Pt electrode in a solution of 0.1 M LiClO₄ in acetonitrile in the presence of 1 mM pyrazine di-N-oxide or its substituted derivatives, 0.5 M cyclohexane and 0.5 M H₂O [19]. The concentration of cyclohexanone was 6-10 times higher than that of cyclohexanol, which was explained by the high rate of 8 × 10⁴ s⁻¹mol⁻¹ [19] for cyclohexanol oxidation to cyclohexanone.

4. Conclusions

In this work, the metal-free electrocatalytic oxidation of cyclohexanol, accompanied by proton elimination, in the presence of Pyr₁, as a mediator, at glassy carbon, SWCNT and MWCNT paper electrodes in a background solution was studied using cyclic voltammetry and quantum chemical modeling. It has been established that the catalytic efficiency of the process at SWCNT and MWCNT paper electrodes is 32 and 20, respectively. This is an order of magnitude higher than that at a glassy carbon electrode. The effects observed in the electrocatalytic systems are explained by quantum-chemical modeling of non-covalent interactions of the components of the studied system with the CNT surface. The high catalytic efficiency of cyclohexanol oxidation at SWCNT and MWCNT paper electrodes indicates the promise of the release of hydrogen evolution at the cathode. The obtained data will allow us to expand the scope of application of catalytic systems aromatic di-N-oxide-CNTs in hydrogen evolution, as well as electrocatalysis, power sources, and sensors. This research is a contribution to the study of the influence of the structure and physicochemical properties of CNTs (promising new electrode materials) on the kinetics and mechanisms of processes occurring on their surface.

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Author Contributions

Dr. Kulakovskaya Svetlana Ivanovna, kulsi@inbox.ru Obtaining experimental data, discussion of the results, preparation and presentation of the published work. Prof. Zyubina Tatyana Sergeevna, zyubin@ipc.ac.ru Quantum Chemical Simulation, discussion of the results. Prof. Zyubin Alexander Sergeevich, zyubinats@bk.ru Quantum Chemical Simulation, discussion of the results. Prof. Kulikov Alexander Vasilevich, kulav1@yandex.ru Obtaining experimental data, discussion of the results. Prof. Dobrovolskiy Yuriy Anatolievich, dobr62@mail.ru Discussion of the results.

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Competing Interests

The authors confirm that there is no conflict of interest related to the manuscript.

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