

Research Article

Role of non-covalent interactions in 2,5-di-Me-pyrazine-di-N-oxide - tertiary butyl alcohol - single-walled and multi-walled carbon nanotubes electrocatalytic systems

Svetlana I. Kulakovskaya*, Tatyana S. Zyubina, Alexander S. Zyubin, Alexander V. Kulikov, Yuriy A. Dobrovolskiy

Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry of the Russian Academy of Sciences, 142432, Chernogolovka, Moscow region, Russia
E-mail: kulsi@icp.ac.ru

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Abstract: Oxidation of tert-butyl alcohol (tert-BuOH, Me₃COH), a compound with a high C-H bond breaking energy in the absence of precious metals or their oxides as catalysts and using metal-free electrodes, is an inexpensive process and is of interest for practical applications in electrocatalysis and sensors.

In this work, electrocatalytic systems 2,5-di-Me-pyrazine-di-N-oxide (Pyr₁) - tert-BuOH – single - walled (SWCNT) and multi-walled (MWCNT) carbon nanotube paper electrodes in 0.1 M Bu₄NClO₄ solution in acetonitrile (MeCN) were studied by the methods of cyclic voltammetry, quantum chemical modeling and electron paramagnetic resonance (EPR) electrolysis. Calculation of energies of non-covalent interactions between the components of the electrocatalytic system in complexes Me₃COH*Me₃COH, Me₃COH*MeCN, Pyr₁*Me₃COH and the adsorption energy of Me₃COH and complexes of Pyr₁*Bu₄NClO₄, Pyr₁*Me₃COH, Pyr₁*MeCN and Me₃COH *Bu₄NClO₄ on CNTs surface using a cluster model describing the surface of conducting carbon nanotubes (10, 10) was performed. The study made it possible to reveal the regularities characteristic of aromatic-di-N-oxide – CNT electrocatalytic systems and to propose a mechanism of tert-BuOH oxidation in the presence of electrochemically generated radical cation Pyr₁. The data will be useful at using CNT electrodes in electrocatalytic processes, as well as aromatic di-N-oxide-CNT catalytic systems in electrocatalysis and sensors.

Keywords: electrocatalysis; carbon nanomaterials; quantum chemical modeling

1. Introduction

Carbon nanomaterials, single-walled and multi-walled nanotubes, nanopaper, and nanofibers are attractive objects both for fundamental research [1–4] and for their use in electronic materials and sensors [5–12] and electrocatalysis [13–22] since they have a high surface area, excellent electronic conductivity, and a wide useful potential window. Investigation of the effect of structure and physicochemical properties of carbon nanomaterials on kinetics and mechanism of electrochemical process at its surface is one of the main goals of the electrochemistry of carbon nanomaterials [1–4]. Single and multi-walled carbon nanotubes modified with organic compounds or metal oxides, are intensively used in electrocatalytic processes [13–22]. Electrocatalytic systems: aromatic di-N-oxides - glassy carbon (GC) - SWCNT and MWCNT carbon nanotube paper electrodes can be

considered as the alternative variants for the catalytic oxidation of organic compounds occurring in the absence of precious metals or their oxides as catalysts and using metal-free electrodes.

It was shown [23–27] that the electrochemically generated at GC and Pt electrodes in 0.1 M LiClO₄ solution in MeCN radical cations of the aromatic di-N-oxide: phenazine-di-N-oxide (PhenDNO, $E_{ox} = +1.23$ V), 2,3,5,6-tetra-Me-pyrazine-di-N-oxide (Pyr₂, $E_{ox} = +1.48$ V), 2,5-di-Me-pyrazine-di-N-oxide (Pyr₁, $E_{ox} = +1.56$ V) and pyrazine-di-N-oxide (Pyr₀, $E_{ox} = +1.63$ V) contain active oxygen in their structures that activates the C-H bond of substrates: alcohols, ethers and cyclohexane. The study [23–27] by the methods of cyclic voltammetry, electron paramagnetic resonance (EPR) electrolysis and quantum chemical modeling made it possible to establish the mechanism of oxidation of aromatic di-N-oxides in the absence and presence of the organic substrate at GC and Pt electrodes in 0.1 M LiClO₄ solution in MeCN. It was assumed that the activation of the C-H bond of the substrate occurs as a result of the electrophilic addition of oxygen of the radical cation of aromatic di-N-oxide to the C-H bond of the substrate and is accompanied by proton elimination and the formation of a radical intermediate, a complex of the radical cation with substrate with the -N-O-C- structure. It was confirmed by registration of radical intermediates by EPR electrolysis at oxidation of phenazine-di-N-oxide in MeOH and its deuterated derivatives [27]. The detection of the same radical intermediate in CH₃OH and CH₃OD proved participation of CH₃ group of alcohol in formation of the intermediate. The mechanism E₁C₁E₂C₂ (where E₁ and E₂ are electrode and C₁ and C₂ are chemical stages of the process) of total two-electron electrocatalytic oxidation of the substrate in a complex with di-N-oxide radical cation with catalysis at the second electrode stage was proposed.

When using SWCNT or MWCNT paper electrodes instead of GC electrode the catalytic efficiency of organic substrate (cyclohexanol, isopropanol and methanol) oxidation increases by several times [28–34]. Feature of the electrocatalytic systems studied in our works [28–34] is the resemblance of the structures of aromatic di-N-oxides and carbon nanotube paper electrodes. This circumstance facilitates adsorption of aromatic di-N-oxides on the surface of CNT paper electrodes. Quantum chemical modeling of the adsorption of Pyr₁ and Fc (ferrocene) reference [32], components of the catalytic system (Pyr₁-MeOH-CNT) and Pyr₁*MeOH complex on CNT surface [33–34] made it possible to explain the effect of increasing the catalytic efficiency of MeOH oxidation at SWCNT and MWCNT paper electrodes in comparison with GC electrode.

Electrochemically generated radical cations Pyr₀ and its substituted Pyr₁ and Pyr₂ have high redox potentials ranging from +1.48 to +1.63 V. This explains their reactivity to the catalytic oxidation of organic compounds with high activation energy of the C-H bond (methanol, cyclohexane). However, an increase in the redox potentials of di-N-oxides is accompanied by the appearance of an irreversible chemical reaction of the radical cation Pyr₀ and its substituted Pyr₁ and Pyr₂ with the solvent. In the presence of organic substrate the radical cation Pyr₀ and its substituted Pyr₁ and Pyr₂ enter into two competing chemical reactions: with organic substrate and an irreversible chemical reaction with MeCN. The existence of a competing reaction with a solvent reduces the catalytic efficiency of the oxidation of an organic substrate.

In this work oxidation of tert-BuOH (C-H bond breaking energy 422.79 kJ/mol) [35] in the presence of the electrochemically generated radical cation Pyr₁ in 0.1 M Bu₄NClO₄ solution in MeCN at SWCNT and MWCNT paper electrodes in comparison with GC electrode were studied by cyclic voltammetry, quantum chemical modeling and EPR electrolysis. The effect of acid (CH₃COOH) and water on this process has also been investigated. Quantum chemical modeling of non-covalent interactions between the components of the electrocatalytic (Pyr₁-tert-BuOH-CNT) system in 0.1 M Bu₄NClO₄ solution in MeCN in complexes Me₃COH*Me₃COH, Me₃COH*MeCN, Pyr₁*Me₃COH and the calculation of the adsorption energy of Me₃COH and complexes of Pyr₁*Bu₄NClO₄, Pyr₁*Me₃COH, Pyr₁*MeCN and Me₃COH*Bu₄NClO₄ on CNTs surface was performed. The study made it possible to establish the effect of non-covalent interactions on the increase in catalytic efficiency of the process and propose the mechanism of electrocatalytic oxidation of tert-BuOH in 0.1 M solution of Bu₄NClO₄ in MeCN at CNT electrodes in the presence of electrochemically generated radical cations Pyr₁. The results of this work will be useful at applying CNT electrodes in electrocatalytic processes, as well as the aromatic di-N-oxide-CNTs catalytic systems in electrocatalysis and sensors.

2. Materials and methods

Materials, experimental techniques for recording cyclic voltammograms (CVs) and EPR spectra during electrolysis at controlled potentials and quantum chemical modeling techniques were described in detail in our previous works [30–32,34].

Acetonitrile and tert-BuOH 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 details in [36].

The CVs were recorded at GC, SWCNT and MWCNT paper electrodes by potentiostat–galvanostat P-40x Elins (Moscow, Russia). A three-electrode cell was used for electrochemical measurements. The visible surface of GC was 0.181 cm². A platinum plate served as the counter electrode. The reference electrode was a silver wire separated from the cell by a bridge filled with 0.1 M Bu₄NClO₄ solution in acetonitrile (this solution was used as a supporting electrolyte in all experiments). The accuracy of the potential recording was ± 0.01 V. Note that before every new experiment the fresh SWCNT and MWCNT paper electrodes were made from the initial material. Before the experiment, GC electrode was polished with micron sandpaper. Then GC and CNTs electrodes were washed by acetone, tridistilled water and dried. During pretreatment of GC, SWCNT and MWCNT paper electrodes, several CVs curves were recorded in the studied potential range in a solution of 0.1 M Bu₄NClO₄ in acetonitrile. Then these electrodes were used in the studied solutions. Before recording each CV in the studied solutions, the electrodes were polarized for 40 s at a voltage of 1.0 V. Before the experiments, oxygen dissolved in solution was removed by bubbling of argon (high purity grade) through the cell. During experiments, the argon flow over solution prevented penetration of oxygen to solution.

The EPR spectra were recorded by a Radiopan spectrometer SE/X 2544 (Poznan) at magnetic field modulation 0.01 mT and microwave power 1 mW. The spectrometer was equipped by a frequency counter and a Tesla meter. The electrochemical EPR cell was similar to that suggested in [37]. A helix of Pt or Au wire ~0.31 mm in diameter served as a working electrode, a cylinder of Pt foil was an auxiliary electrode, and silver wire was the reference electrode. The cell was inserted into resonator of the EPR spectrometer and EPR spectra were recorded during electrolysis at controlled potentials. During EPR spectrum recording at low temperatures, the cell was inserted into a quartz tube with flow of nitrogen with required temperature.

Electrodes from carbon nanopaper were obtained as described in [38]. 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 thickness of 0.1 mm. According to our data of scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM) [31], nanopaper contains multi-walled carbon nanotubes with diameter of ~20 nm and length of ~2 μm. SWCNTs for the preparation of nanopaper were produced in our Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, RAS by the electric arc method using the Ni/Y catalyst. Nanopaper was a thin layer of black paper-like material with a thickness of 0.03–0.04 mm, which contained 90% nanotubes and less than 0.5% metals. According to the scanning electron microscopy data, the nanopaper consists of bundles with a ribbon structure, including 500–10 000 SWCNTs with a typical diameter of ~1.4 nm.

For theoretical calculations, (10, 10) CNTs with a diameter equal to the average experimental diameter of 1.36 nm were chosen. Since experimental studies have shown that in the case of MWCNTs (~20 nm in diameter) the result does not qualitatively change when going from SWCNTs (~1.4 nm in diameter) to multilayer tubes (but the calculation time depends on this), the calculation was limited to single-layer tubes.

The adsorption of components of catalytic system tert-BuOH-Pyr₁ in 0.1 M Bu₄NClO₄ solution in MeCN on the nanotube surface and their mutual interactions was modeled using a hybrid density functional ωB97XD [39–40]) with taking into account dispersion interactions. As basis sets were used widespread 6-31G(d, p), more complicated 6-311G (d, p) and aug-cc-pVTZ bases.

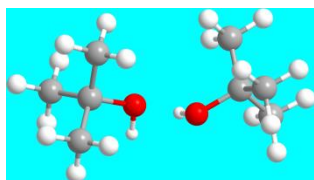
Infinite nanotube (10, 10) CNT was optimized in frame method with periodic boundary conditions, approach with the PBE hybrid density functional [41] and the projector augmented wave (PAW) [42]. The calculations were made with Vienna Ab initio Simulation Package (VASP) [43–46]. The energy limit, which determines the completeness of the basis set, was taken equal to 400 eV. The obtained geometric parameters were further used to construct the C₅₄H₁₈ cluster as models of CNTs surface because in our previous work [32] it was shown to be a suitable model. Coordinates of carbon atoms in the model cluster C₅₄H₁₈ were taken from an optimized nanotube structure (within the framework of PBE/PAW), dangling boundary bonds were closed by H atoms. Optimization of the geometry of the combined system (model cluster with adsorbed molecules) was carried out at fixed coordinates of the model cluster C₅₄H₁₈ (to preserve the surface shape). The positions of carbon and hydrogen atoms in the cluster are fixed on those obtained from free (10, 10) CNT and only the positions of adsorbed molecules were optimized [32–34] on the ωB97XD/6-31G (d,p) level.

After optimization the energetic values were refined on the ωB97XD/6-311G(d,p) level with account of basis set superposition error (BSSE). It is need to point out that these values obtained at ωB97XD/aug-cc-pVTZ level are 2–4 kcal/mol less than those obtained at ωB97XD/6-311G(d,p) and ωB97XD//6-31G(d,p) levels, but the trends in the series are identical for all considered approaches. The calculations were made on computational centre of FRC PCP MC RAS with using of the GAUSSIAN 09 software package [47].

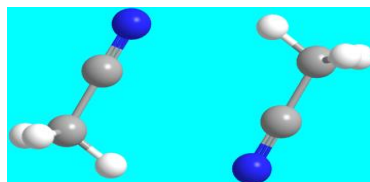
Simulation of solvent (acetonitrile) influence was made by means of Self-Consistent Reaction Field (SCRF) method in frame of Integral Equation Formalism with Polarizable Continuum Model approach (IEFPCM). The appropriate data are presented in Tabl.1 and Fig.1 and are marked with the index "s". However, this modification

of calculation method does not change calculated structural and energetic parameters essentially, binding energy of the complexes decreases by 1–3 kcal/mol, which do not lead to qualitative changes into the conclusions made in the article.

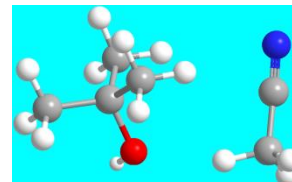
The binding energy of non-covalent interactions (E_b) is defined as the difference $E_b = E_{A*B} - (E_A + E_B)$, where E_{A*B} is the energy of the A*B cluster, and E_A and E_B are the energies of monomers A and B, respectively. Negative value of E_b indicates the presence of a bond in the complex, and a positive value indicates its absence.



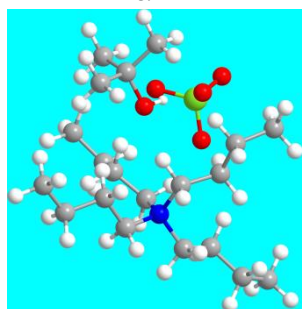
1. Me₃COH*Me₃COH
-11.7⁽¹⁾, -10.1⁽¹⁾, -11.4⁽³⁾,
-8.1⁽⁴⁾



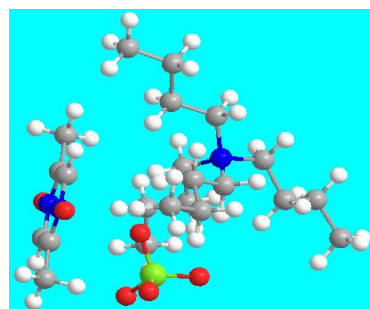
2. MeCN*MeCN
-7.2⁽¹⁾, -6.3⁽²⁾, -7.2⁽³⁾, -6.4⁽⁴⁾



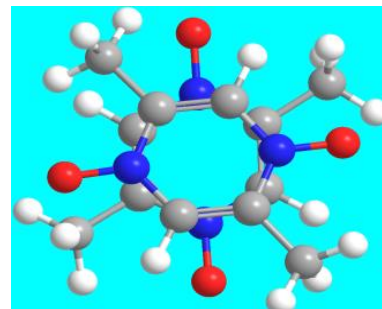
3. Me₃COH*MeCN
-7.0⁽¹⁾, -10.1⁽¹⁾, -6.8⁽³⁾, -5.4⁽⁴⁾



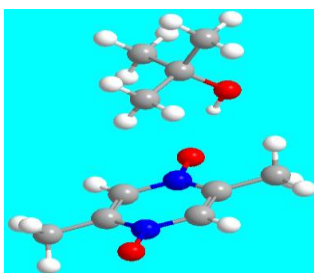
4. Me₃COH*Bu₄NClO₄
-20.3⁽¹⁾, -13.7⁽¹⁾, -24.5⁽³⁾, -19.7⁽⁴⁾



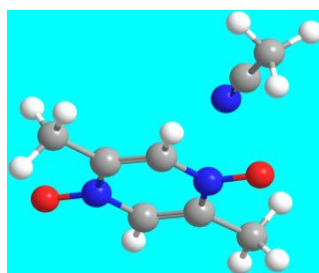
5. Pyr₁*Bu₄NClO₄
-17.3⁽¹⁾, -12.8⁽¹⁾, -19.0⁽³⁾, -14.1⁽⁴⁾



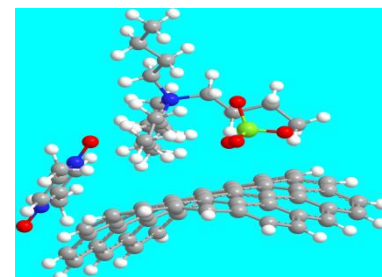
6. Pyr₁*Pyr₁
-15.8⁽¹⁾, -12.9⁽²⁾, -19.31⁽³⁾, -13.97⁽⁴⁾



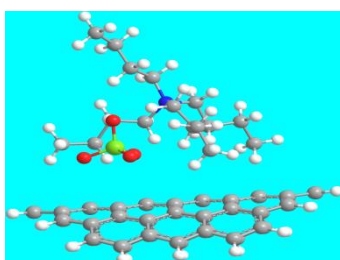
7. Pyr₁*Me₃COH
-13.4⁽¹⁾, -11.5⁽¹⁾, -13.7⁽³⁾, -10.3⁽⁴⁾



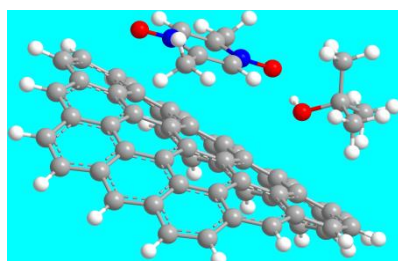
8. Pyr₁*MeCN
-8.6⁽¹⁾, -5.1⁽¹⁾, -6.9⁽²⁾, -8.6⁽³⁾, -6.9⁽⁴⁾



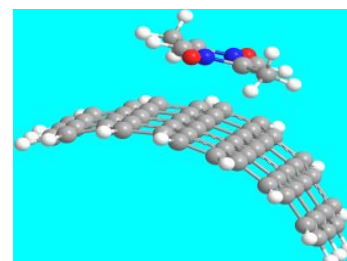
9. Pyr₁*Bu₄NClO₄*CNT
-28.8⁽¹⁾, -28.7⁽³⁾, -23.9⁽⁴⁾



10. Bu₄NClO₄*CNT
-21.5⁽¹⁾, -19.2⁽¹⁾, -22.9⁽³⁾,
-18.9⁽⁴⁾



11. Pyr₁*Me₃COH*CNT
-20.69⁽¹⁾, -16.2⁽¹⁾, -21.3⁽³⁾, -16.1⁽⁴⁾



12. Pyr₁*CNT
-17.1⁽¹⁾, -16.1⁽¹⁾, -18.2⁽³⁾, -14.5⁽⁴⁾

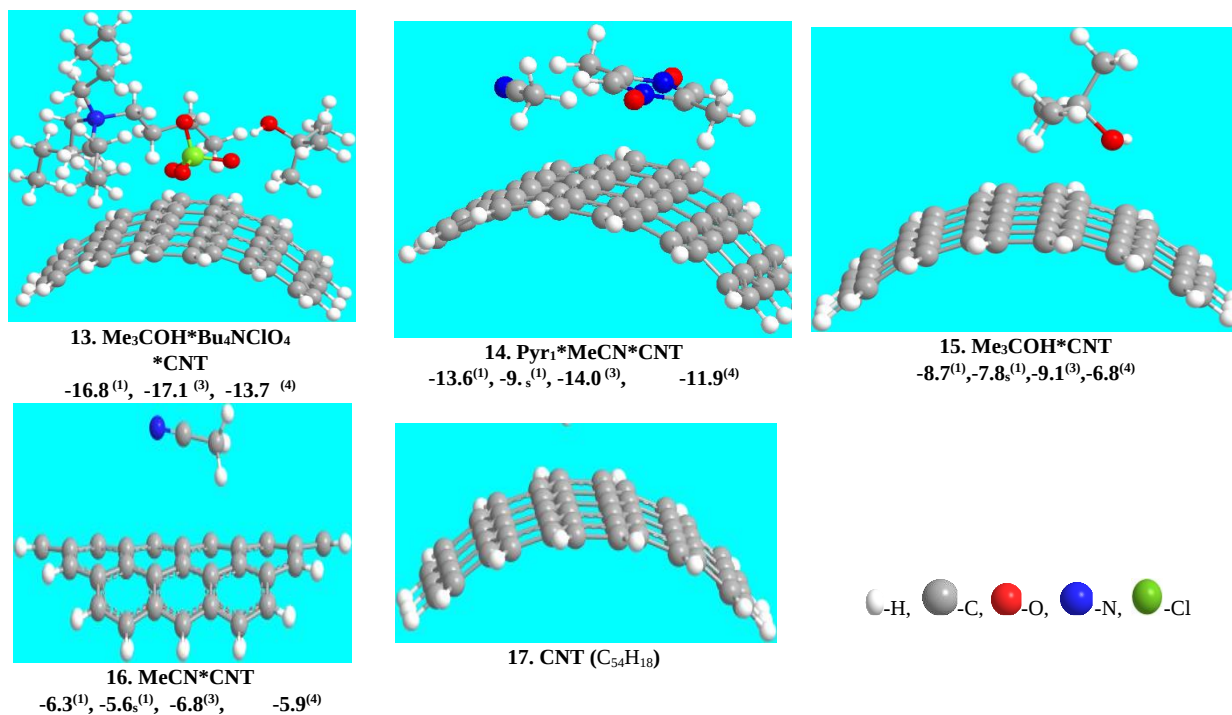


Figure 1. Structure and binding energies (E_b , kcal/mol) in complexes. The SCF levels of calculation are given: ⁽¹⁾wB97XD//6-31G(d,p), ⁽²⁾wB97XD/aug-cc-pVTZ, ⁽³⁾wB97XD//6-31G(d,p)//6-311G(d,p), ⁽⁴⁾wB97XD/6-31G(d,p)//6-311G(d,p)(BSSE), s - solvent accounting by SCRF method

Table 1. Binding energies (E_b , kcal/mol) in complexes obtained at different calculation levels*)

Complex	Method	E_b
1. Me₃COH*Me₃COH	SCF	-11.70 ⁽¹⁾ , -10.12 ⁽¹⁾ , -11.41 ⁽³⁾ , -8.11 ⁽⁴⁾
	ZPE	-9.57 ⁽¹⁾ , -8.05 ⁽¹⁾
	H	-9.57 ⁽¹⁾ , -8.06 ⁽¹⁾
	G	1.38 ⁽¹⁾ , 2.93 ⁽¹⁾
4. Me₃COH*Bu₄NClO₄	SCF	-20.32 ⁽¹⁾ , -13.68 ⁽¹⁾ , -24.46 ⁽³⁾ , -19.70 ⁽⁴⁾
	ZPE	-18.44 ⁽¹⁾ , -12.30 ⁽¹⁾
	H	-18.35 ⁽¹⁾ , -12.03 ⁽¹⁾
	G	-5.81 ⁽¹⁾ , -0.29 ⁽¹⁾
7. Pyr₁* Me₃COH	SCF	-13.39 ⁽¹⁾ , -11.49 ⁽¹⁾ , -13.69 ⁽³⁾ , -10.32 ⁽⁴⁾
	ZPE	-11.54 ⁽¹⁾ , -9.44 ⁽¹⁾
	H	-11.43 ⁽¹⁾ , -9.45 ⁽¹⁾
	G	-0.54 ⁽¹⁾ , 2.15 ⁽¹⁾

*) The 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). The accepted designations: SCF - Self-consistent energy, ZPE - Zero-point Energy, H - Thermal

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 Fig.1 and Table1. The absolute value of the binding energy in the series complexes changes according to the following sequences: a) **1.** $\text{Me}_3\text{COH} \cdot \text{Me}_3\text{COH} > \textbf{2.}$ $\text{MeCN} \cdot \text{MeCN}$ [34] $> \textbf{3.}$ $\text{Me}_3\text{COH} \cdot \text{MeCN}$; b) with Bu_4NClO_4 : **4.** $\text{Me}_3\text{COH} \cdot \text{Bu}_4\text{NClO}_4$; c) with Pyr_1 : **5.** $\text{Pyr}_1 \cdot \text{Bu}_4\text{NClO}_4$ [34] $> \textbf{6.}$ $\text{Pyr}_1 \cdot \text{Pyr}_1$ [34] $> \textbf{7.}$ $\text{Pyr}_1 \cdot \text{Me}_3\text{COH} > \textbf{8.}$ $\text{Pyr}_1 \cdot \text{MeCN}$ [34]; d) with CNT: **9.** $\text{Pyr}_1 \cdot \text{Bu}_4\text{NClO}_4 \cdot \text{CNT} > \textbf{10.}$ $\text{Bu}_4\text{NClO}_4 \cdot \text{CNT}$ [34] $> \textbf{11.}$ $\text{Pyr}_1 \cdot \text{Me}_3\text{COH} \cdot \text{CNT} > \textbf{12.}$ $\text{Pyr}_1 \cdot \text{CNT}$ [32] $> \textbf{13.}$ $\text{Me}_3\text{COH} \cdot \text{Bu}_4\text{NClO}_4 \cdot \text{CNT} > \textbf{14.}$ $\text{Pyr}_1 \cdot \text{MeCN} \cdot \text{CNT} > \textbf{15.}$ $\text{Me}_3\text{COH} \cdot \text{CNT} > \textbf{16.}$ $\text{MeCN} \cdot \text{CNT}$ [32].

3.2 Oxidation of Pyr_1 at GC, SWCNT and MWCNT paper electrodes in MeCN

3.2.1 In the absence of *tert*-BuOH

Previously [32] the oxidation of Pyr_1 and Fc in 0.1 M Bu_4NClO_4 solution in MeCN at GC and SWCNT and MWCNT paper electrodes was studied by the methods of cyclic voltammetry, EPR electrolysis, and quantum chemical modeling. It was shown that the oxidation of Fc at GC, SWCNT, and MWCNT electrodes is one-electron, reversible, and diffusion-controlled; therefore, Fc can be used as a reference when studying electrode processes at these electrodes. The oxidation of Pyr_1 [32] is one-electron, irreversible, diffusion-controlled and the charge transfer is followed by irreversible chemical reaction with the solvent (EC mechanism [48] where E is electrode and C is chemical stages of process) with the rate constant equal to 0.6 s^{-1} . Cyclic voltammograms (CV) of the oxidation of Pyr_1 and Fc in 0.1 M Bu_4NClO_4 solution in MeCN at GC, SWCNT and MWCNT paper electrodes at different potential scan rates are shown in Fig. 2. The data obtained in this work (Fig. 2) and in work [32] are in good agreement. The recording of the EPR spectrum of the radical cation Pyr_1 in [32] during electrolysis at Pt electrode at +1.6 V in 0.1 M LiClO_4 solution in MeCN at -40°C serves as proof of one electron oxidation of Pyr_1 . The intensity of the EPR spectrum of the radical cation Pyr_1 reached a maximum at +1.6 V and then remained unchanged up to +2.4 V. This indicates that there is no further oxidation of the Pyr_1 radical cation to a dication in the studied potential region.

Similarly to the work [32], oxidation of Pyr_1 at MWCNT and SWCNT paper electrodes (Fig. 2b, c) in 0.1M Bu_4NClO_4 solution in MeCN occurs at a potential of 1.78 V, which is 220 mV higher than the oxidation potential of Pyr_1 at GC electrode. The process is irreversible and not diffusion-controlled. In contrast to the GC electrode (Fig. 2a), the oxidation currents of 1 mM Pyr_1 at MWCNT and SWCNT paper electrodes (Fig. 2b, c) are several times higher than the diffusion oxidation current of 1 mM Fc. By quantum-chemical modeling of the adsorption of Pyr_1 and Fc on CNT electrodes it was shown in [32] that the adsorption energy of Pyr_1 on CNT electrodes, in contrast to Fc, exceeds the adsorption energy of solvent molecules MeCN displaced from the CNT surface. Due to the adsorption of Pyr_1 , its concentration on the CNT surface and its oxidation current increase compared to the GC electrode.

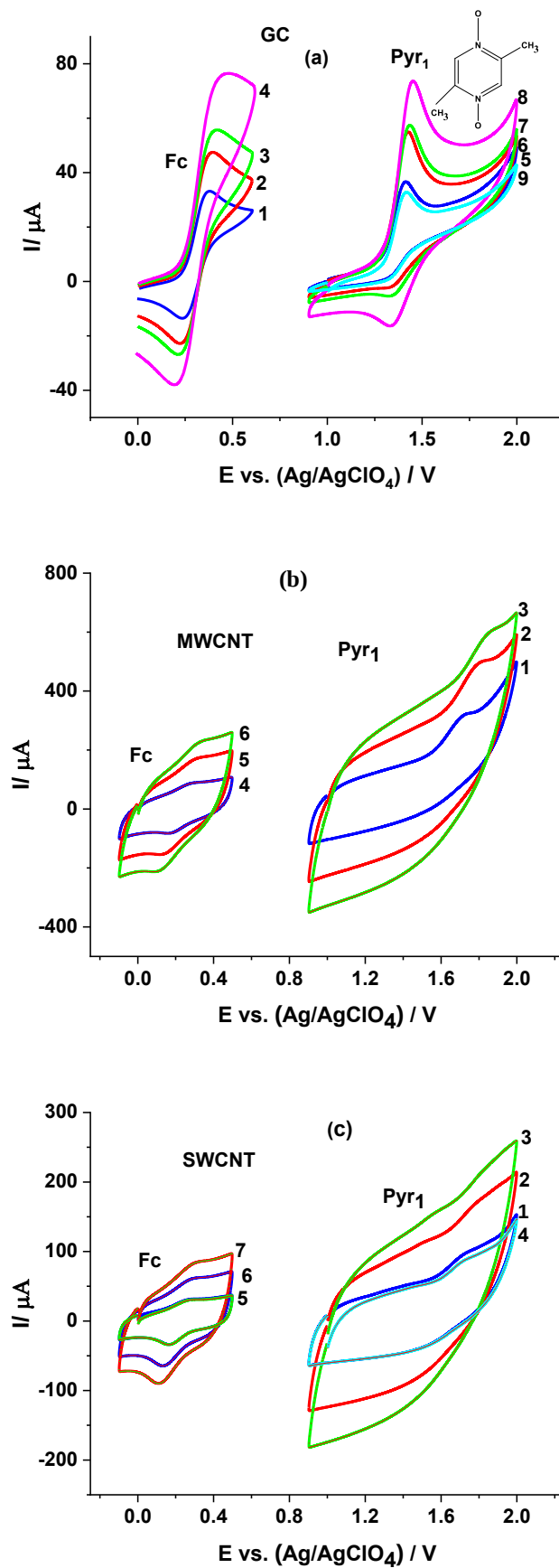
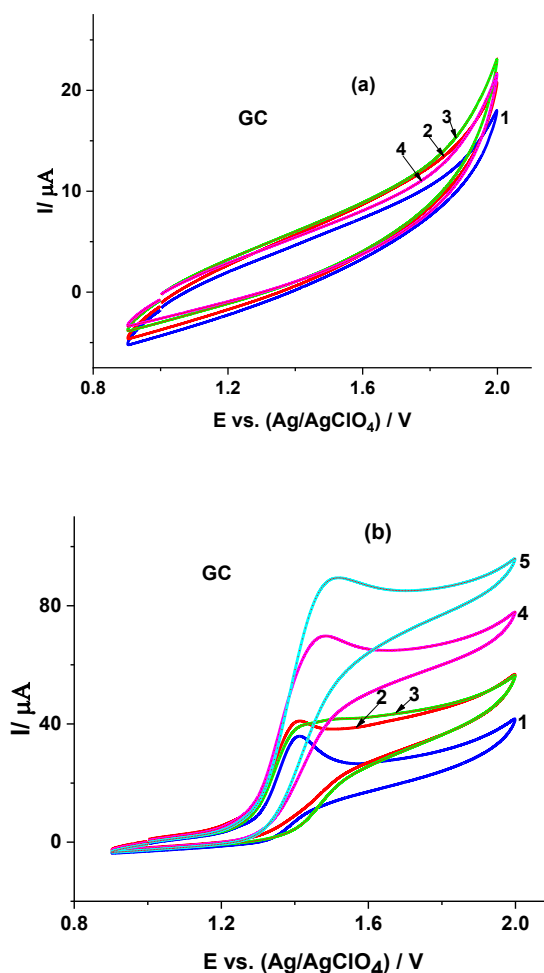
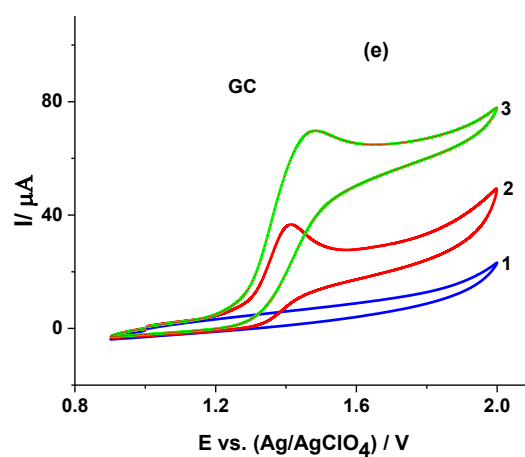
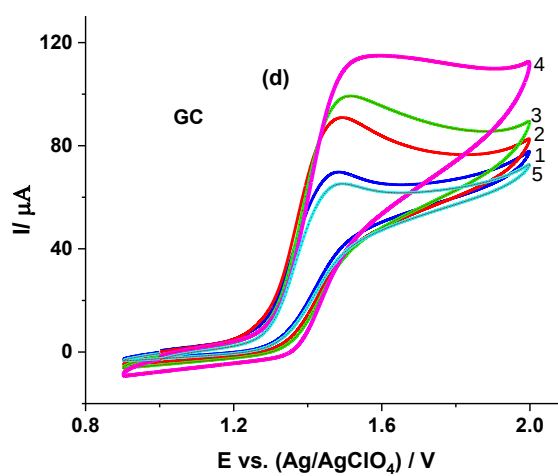
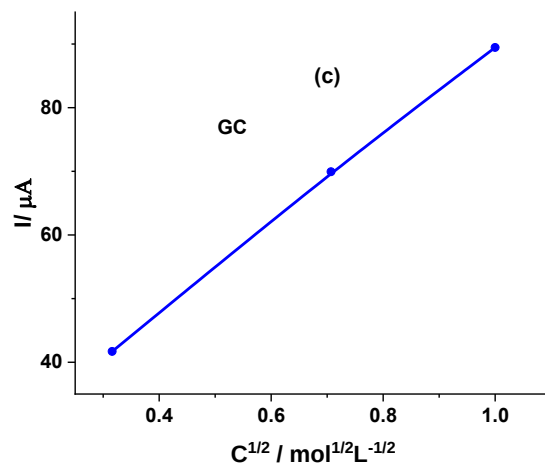


Figure 2. CVs of 0.1 M Bu_4NClO_4 solution in acetonitrile at (a) GC and (b) MWCNT (c) SWCNT paper electrodes in the presence of (1 – 4) 1 mM Fc and (5 – 9) 1 mM Pyr₁ at a potential scan rate (1, 5, 9) – 20 mV/s; (2, 6) – 50 mV/s; (3, 7) – 80 mV/s; (4, 8) – 200 mV/s

3.2.2 In the presence of *tert*-BuOH

In the absence of Pyr₁, oxidation of *tert*-BuOH at Gc electrode in 0.1 M Bu₄NClO₄ solution in MeCN is not observed when *tert*-BuOH concentration changes from 0.1 to 1.0 M (Fig. 3a). The oxidation current of 1 mM Pyr₁ increases (Fig. 3b) at addition of 0.05 - 1.0 M *tert*-BuOH and becomes catalytic at concentrations of 0.5 M *tert*-BuOH and higher. Note that, unlike other substrates, the catalytic oxidation of *tert*-BuOH with the participation of electrochemically generated radical cations of pyrazine-di-N-oxide and its substituted derivatives is observed at potentials close to the oxidation potentials of the initial pyrazine-di-N-oxides. This fact was registered both in the previous work [49] at GC and Pt electrodes in 0.1 M LiClO₄ solution in MeCN, and in this work at the GC electrode in 0.1 M Bu₄NClO₄ solution in MeCN. This indicates that the oxidation potentials of di-N-oxides and complexes of their radical cations with *tert*-BuOH are close. According to [48], the catalytic nature of the current is evidenced by the linear dependence of I_{cat} on the square root of the *tert*-BuOH concentration (Fig. 3c) and a weak dependence on the potential scan rate (Fig. 3d). The catalytic efficiency of the process at GC electrode in the the presence of 1 mM Pyr₁ and 0.5 M *tert*-BuOH in 0.1 M Bu₄NClO₄ solution in MeCN (Fig. 3e) is equal to 2. The catalytic efficiency α was defined as the ratio of the catalytic oxidation current of di-N-oxide in the presence of organic substrate to the current diffusion of Fc, reference. Note that in the presence of 0.5 M *tert*-BuOH, the catalytic current increases in 1.5 times with a doubling of the Pyr₁ concentration (Fig. 3f).





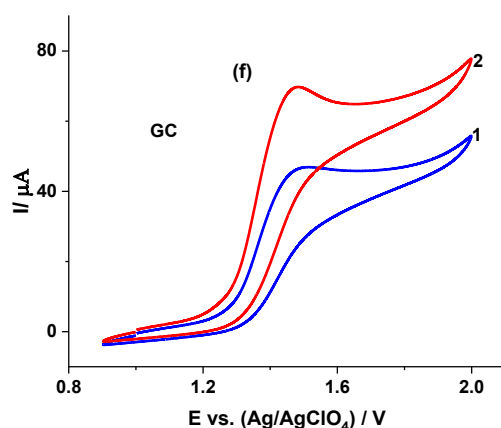
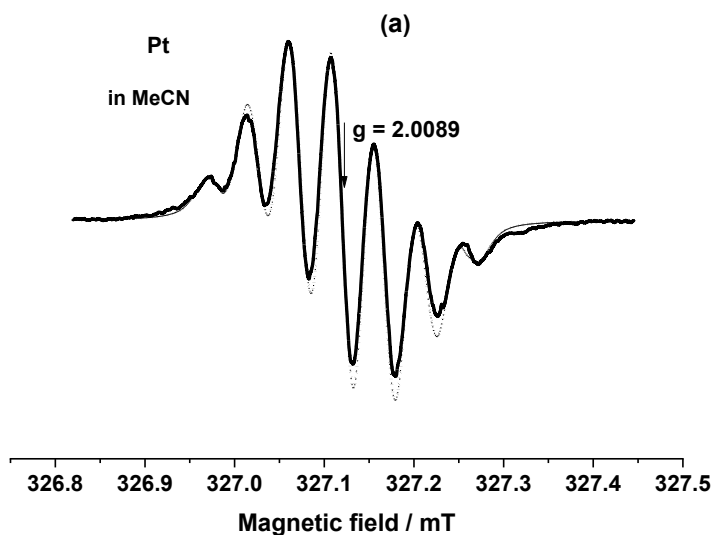


Figure 3. CVs of 0.1 M Bu_4NClO_4 solution in acetonitrile at GC electrode at a potential scan rate of 20 mV/s in the presence of *tert*-BuOH: (a) (1) 0, (2) 0.1, (3) 0.5, (4) 1.0 M; (b) 1 mM Pyr_1 and *tert*-BuOH: (1) 0, (2) 0.1, (3) 0.5, (4) 1.0 M; (c) dependence of the anodic peak current on the square root of the *tert*-BuOH concentration: (d) 1 mM Pyr_1 and 0.5 M *tert*-BuOH at potential scan rate: (1) 20, (2) 50, (3) 80, (4) 200 mV/s; (e) (1) 0.1 M Bu_4NClO_4 and 0.5 M *tert*-BuOH; (2) 1 mM Pyr_1 ; (3) 1 mM Pyr_1 and 0.5 M *tert*-BuOH; (f) 0.5 M *tert*-BuOH and Pyr_1 : (1) 0.5 mM and (2) 1 mM Pyr_1 at potential scan rate 20 mV/s

It was previously found [49] that the EPR spectrum of the Pyr_1 radical cation (Fig. 4a) recorded at electrolysis at +1.6 V at Pt electrode at temperature of -45°C in 0.1 M LiClO_4 solution in MeCN in the absence of a substrate disappears at the addition of *tert*-BuOH. This indicated an interaction of the radical cation with *tert*-BuOH. EPR spectra of the Pyr_1 radical cation at +1.5 V (Fig. 4b) and the radical anion at -0.4 V (Fig. 4c) were recorded in [49] at Au electrode during electrolysis in 0.05 M LiClO_4 solution in *tert*-BuOH used simultaneously as solvent and substrate, at temperature of *tert*-BuOH melting point $+25^\circ\text{C}$ [50]. The EPR spectra were simulated in [49], and their parameters are presented in Table 2. No new spectra were recorded in the potential range from -1.1 to $+2.5$ V. The identity of the EPR spectra of the 1 mM Pyr_1 radical cation recorded at Pt electrode in the absence of a substrate in 0.1 M LiClO_4 solution in MeCN (Fig. 4a) and at Au electrode in 0.05 M LiClO_4 solution in *tr*-BuOH confirmed the catalytic nature of the process.



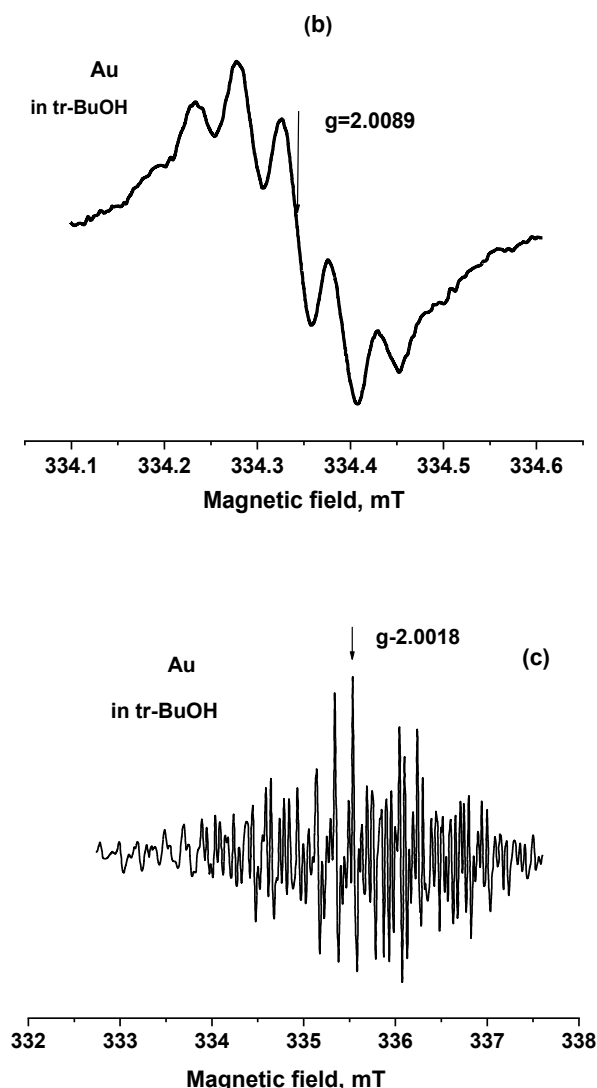


Figure 4. EPR spectra recorded at electrolysis of 1 mM Pyr₁ solution (a) in MeCN containing 0.1 M LiClO₄ at Pt electrode at temperature of –45 °C and potential of +1.6 V; and in tert-BuOH containing 0.05 M LiClO₄ at Au electrode at temperature of 25 °C and potentials: (b) +1.5 V and (c) –0.4 V. Dotted lines are calculated by the parameters given in Tables 2

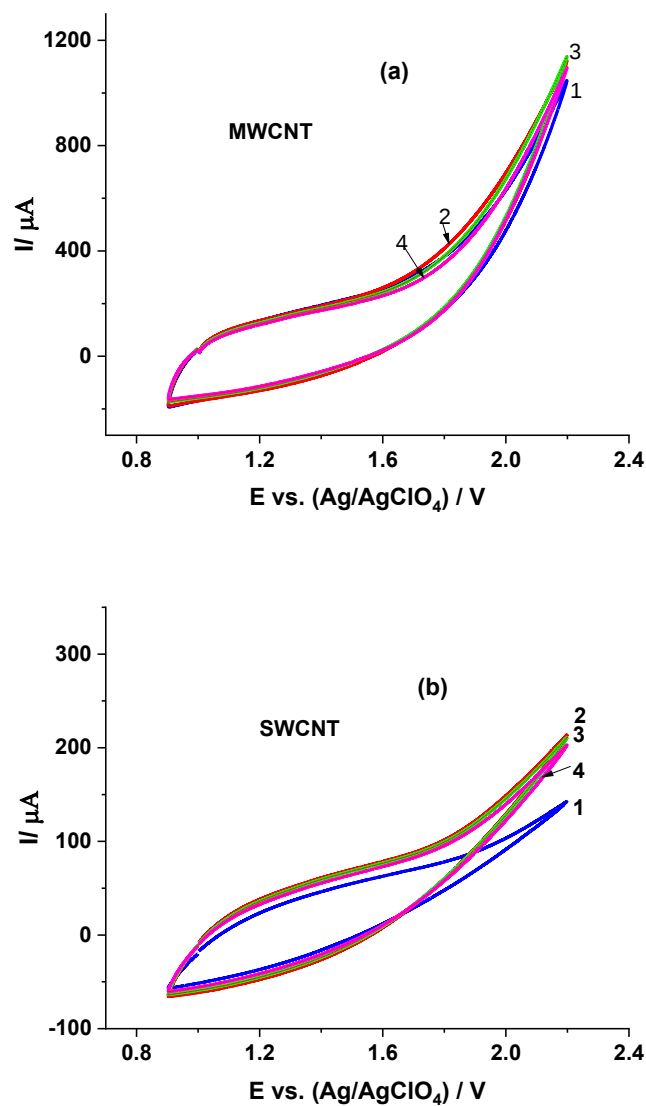
Table 2. EPR spectral parameters of Pyr₁ radical cation in MeCN and in tert-BuOH

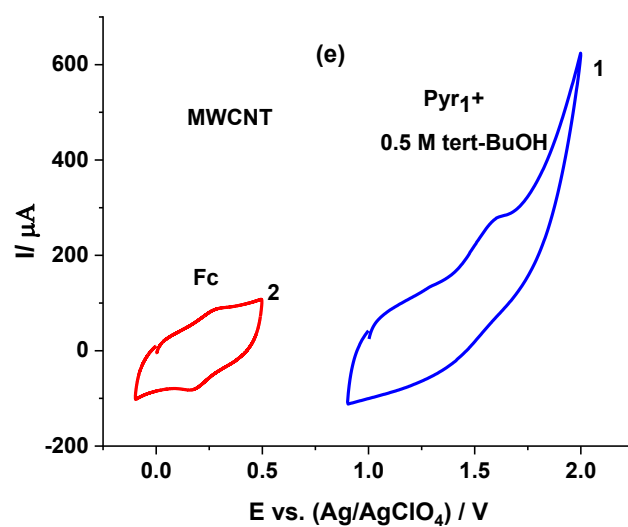
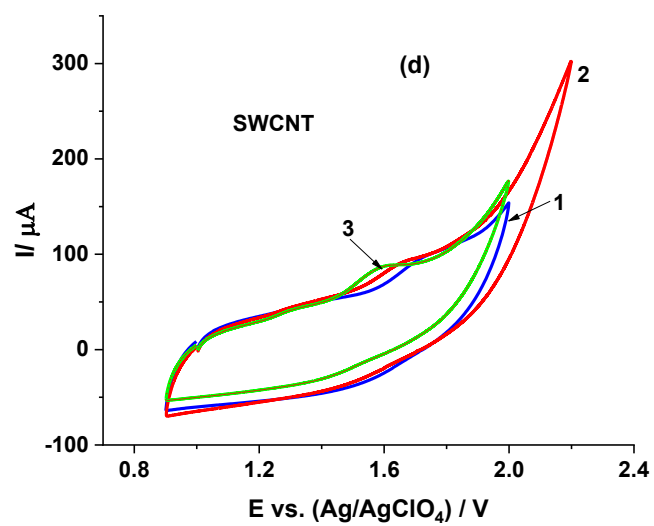
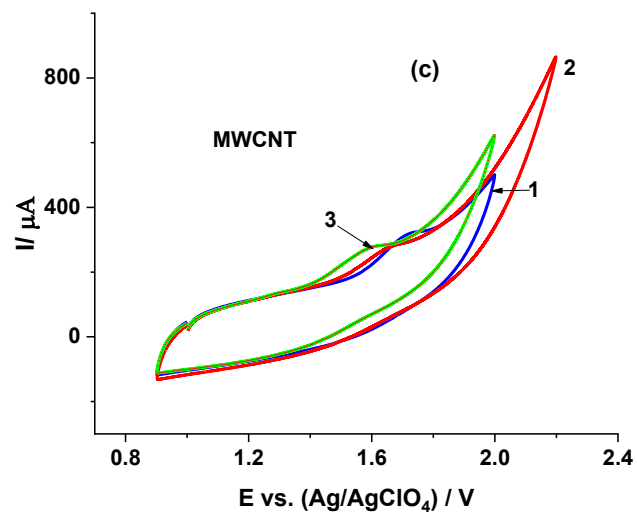
Solvent	g-factor	Hyperfine structure constants (<i>a</i> , mT) and number of equivalent nuclei (<i>n</i>)						ΔH , mT**
		<i>a</i> _{H1} , mT	<i>n</i> _{H1}	<i>a</i> _{H2} , mT	<i>n</i> _{H2}	<i>a</i> _N , mT	<i>n</i> _N	
MeCN	2.0089	0.042	2	0.0094	6	0.047	2	0.012
tert-BuOH	2.0089	0.042	2	0.0094	6	0.047	2	0.012

** Half width at half height of Lorentz line

In the absence of Pyr₁ at CVs obtained at MWCNTs and SWCNTs paper electrodes in 0.1 M Bu₄NClO₄ solution in MeCN in the presence of tert-BuOH at a concentration from 0.1 to 1.0 M, no oxidation of tert-BuOH was registered (Fig. 5a, b). When 0.1- 0.5 M tert-BuOH is added to 0.1 M Bu₄NClO₄ solution in MeCN, the CVs of Pyr₁ oxidation at CNT paper electrodes shift towards lower positive potentials (Fig. 5c, d). Note that the peak currents at these CVs are several times higher than the oxidation current of Fc (Fig. 5e, f). The peak currents weakly depend on the potential scan rate (Fig. 6a, b) and increase in proportion to the increase in Pyr₁ concentration in the range from 0.5 to 1.0 mM (Fig. 6c, d). All these factors point to the catalytic nature of the recorded currents. The catalytic efficiency of tert-BuOH oxidation in the presence of 1 mM Pyr₁ and 0.5 M tert-

BuOH in 0.1 M Bu₄NClO₄ solution in MeCN at MWCNT and SWCNT paper electrodes is 3 and 4, respectively, using Fc as a reference. Thus, the catalytic efficiency of tert-BuOH oxidation increases at MWCNT and SWCNT paper electrodes by factors of 1.5 and 2, respectively, compared to GC electrode.





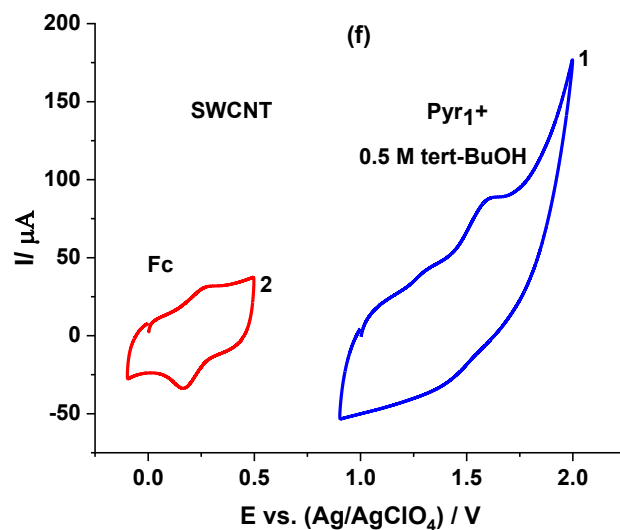
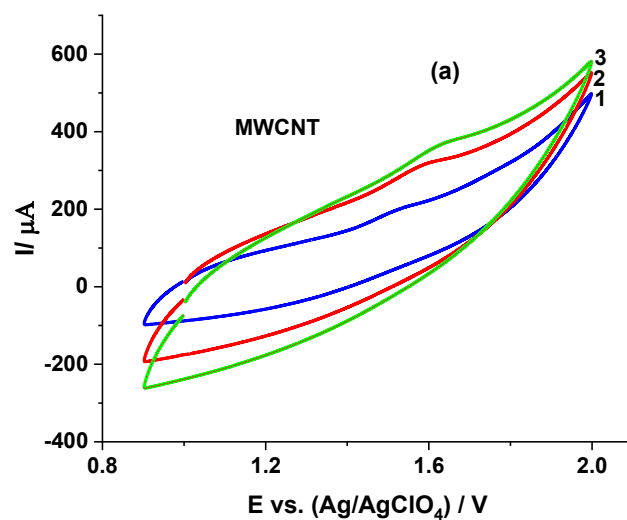


Figure 5. CVs of 0.1 M Bu_4NClO_4 solution in MeCN at a potential scan rate of 20 mV/s in the presence of tert-BuOH: (1) 0, (2) 0.1, (3) 0.5, (4) 1.0 M at (a) MWCNT and (b) SWCNT paper electrodes; in the presence of 1 mM Pyr_1 and tert-BuOH: (1) 0, (2) 0.1, (3) 0.5 at (c) MWCNT and (d) SWCNT paper electrodes; in the presence of (1) 1 mM Pyr_1 and 0.5 M tert-BuOH, (2) 1mM Fc at (e) MWCNT and (f) SWCNT paper electrodes



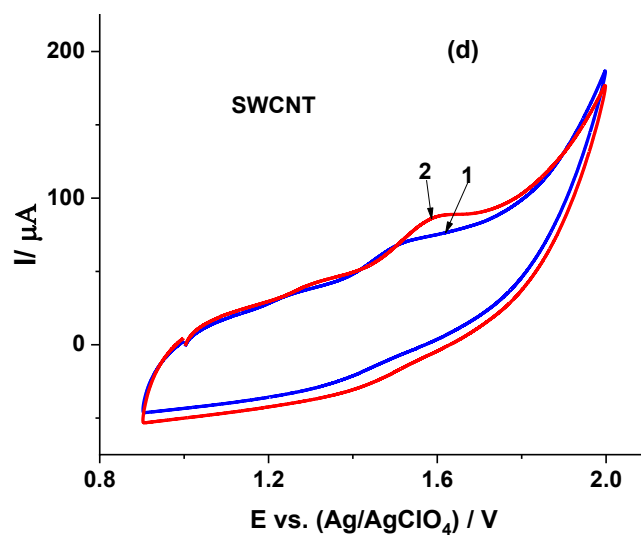
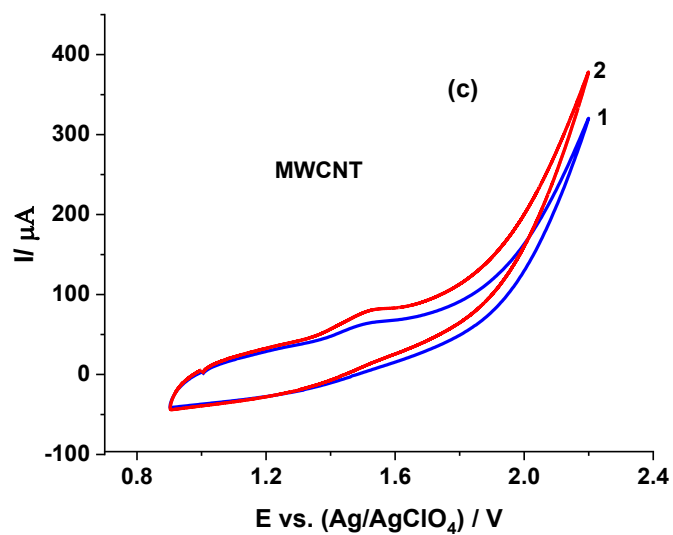
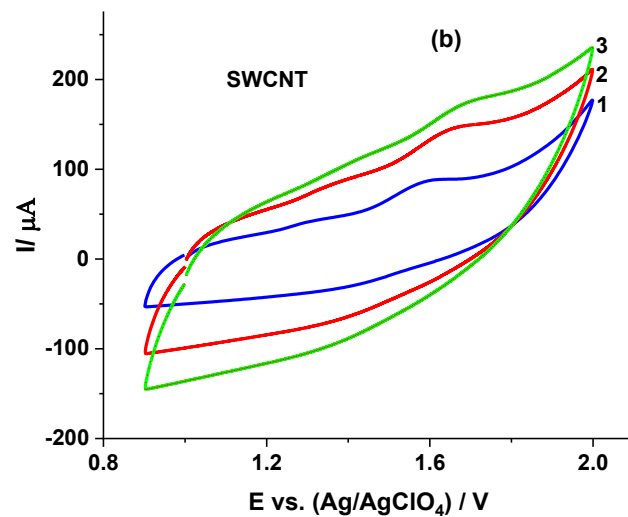


Figure 6. CVs of 0.1 M Bu₄NClO₄ solution in MeCN in the presence of 1 mM Pyr₁ and 0.5 M tert-BuOH at a potential scan rate: (1) 20, (2) 50, (3) 80 mV/s at (a) MWCNT and (b) SWCNT paper electrodes; in the presence of 0.5 M tert-BuOH and Pyr₁: (1) 0.5 mM, (2) 1 mM at a potential scan rate of 20 mV/s at (c) MWCNT and (d) SWCNT paper electrodes

From quantum chemical modeling of the energy of non-covalent interactions between the components of the catalytic system Pyr₁-tert-BuOH in 0.1 M Bu₄NClO₄ solution in MeCN and the adsorption of components at CNTs follows (Fig. 1, Table 1):

- 1. The studied solutions contain** Me₃COH*Bu₄NClO₄ and Pyr₁*Bu₄NClO₄ complexes with non-covalent interaction energies of -19.7⁽⁴⁾ and -14.1⁽⁴⁾ kcal/mol, respectively.
- 2. On the uncharged surface of CNTs electrodes** Pyr₁*Bu₄NClO₄*CNT complex will be present, since its adsorption energies, equal -23.9⁽⁴⁾ kcal/mol exceeds the adsorption energies of other components of the catalytic system (Fig. 1).
- 3. On the positively charged surface of CNTs electrodes** ClO₄⁻ anions will be present, the adsorption of Bu₄N⁺ cations is impossible. Therefore Pyr₁*Bu₄NClO₄*CNT and Bu₄NClO₄*CNT complexes will be absent on their surface. The Pyr₁*Me₃COH*CNT complex will be adsorbed on the positively charged surface of CNTs electrodes and participate in the catalytic process of tert-BuOH oxidation.

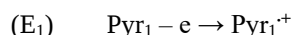
Since the adsorption energy of the Pyr₁*Me₃COH*CNT (-16.1⁽⁴⁾ kcal/mol) complex exceeds the adsorption energy of the Pyr₁*MeCN*CNT (-11.9⁽⁴⁾ kcal/mol) and MeCN*CNT (-5.9⁽⁴⁾ kcal/mol) complexes (Fig. 1, Table 1), the concentration of the catalytically active Pyr₁*Me₃COH*CNT complex will dominate on the CNT surface. Adsorption of the complex of di-N-oxide with tert-BuOH leads to an increase in the concentration of catalytically active species on the surface of CNTs electrodes compared to the GC electrode. As a result, the catalytic efficiency of the process on CNTs electrodes will exceed the catalytic efficiency of the process on the GC electrode.

The concentrations of the Pyr₁*MeCN*CNT and MeCN*CNT complexes on the CNT surface will be negligible and, consequently, the occurrence of a competing chemical reaction of the Pyr₁ radical cation with MeCN on the CNT electrodes will be unlikely. These factors lead to an increase in the catalytic efficiency of the process at CNTs electrodes compared to GC electrode. A similar effect was observed in [34] when studying the oxidation of Pyr₁ in the presence of MeOH at SWCNT and MWCNT paper electrodes.

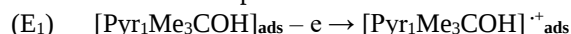
According to E₁C₁E₂C₂ mechanism of total two-electron electrocatalytic oxidation of the substrate in a complex with di-N-oxide radical cation proposed earlier in [23–27], the process of complex formation (stage C₁) and regeneration of the initial di-N-oxide (stage C₂) are accompanied by proton elimination. Therefore, the presence of water as a base will accelerate the catalytic process, while the presence of an acid will inhibit it. It follows from the obtained data that the presence of water (Fig. 7a, b) leads to an increase in catalytic currents, the presence of acid (CH₃COOH) (Fig. 8a, b) to the inhibition of the catalytic process both at GC and at CNTs paper electrodes. Note that the catalytic effect of water is more pronounced at the GC electrode (increase in the catalytic current by 1.5 times) than on the CNTs electrodes. This effect is explained by quantum chemical modeling [33], according to which the adsorption energy of water on CNTs electrodes (3 kcal mol⁻¹) is much lower and insufficient to displace MeCN solvent (adsorption energy 5.9 kcal mol⁻¹) and other components of the catalytic system (Fig. 1, Table 1) from the CNTs surface. In comparison with GC electrode the inhibitory effect of CH₃COOH is higher at CNTs electrodes (Fig. 1, Table 1), since the adsorption energy of CH₃COOH on CNTs electrodes (6.3 kcal mol⁻¹) [33] is sufficient to displace MeCN molecules from the CNTs electrodes surface. The acid concentration increases at the CNTs electrodes surface compared to the solution, and the inhibitory effect is stronger. The obtained dependences of the catalytic current on the presence of water and acid confirm that the catalytic process proceeds with protons elimination. Based on the study, the following mechanism of Pyr₁ oxidation in the presence of tert-BuOH at MWCNT and SWCNT paper electrodes can be proposed.

E₁—first electrode stage

At GC electrode Pyr₁ is oxidized to the radical cation. The process is one-electron, irreversible, diffusion-controlled.

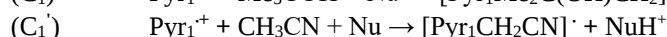


At SWCNT and MWCNT paper electrodes [Pyr₁Me₃COH]_{ads} complex adsorbed on the CNT surface is oxidized to the radical cation. This process is irreversible and not controlled by diffusion.

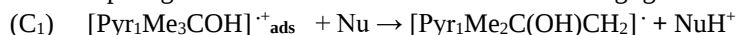


C₁—first chemical stage.

At GC electrode at the first chemical stage two competitive chemical reactions of the electrophilic addition of the oxygen atom of Pyr₁ radical cations to the C-H bonds of Me₃COH and MeCN occur. The reactions are accompanied by proton elimination and the formation of radical intermediates (complexes with an N-O-C structure). Compounds of this structure and methods for their preparation are known [51–57].

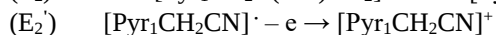
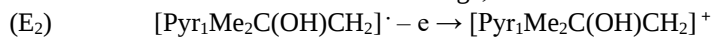


At SWCNT and MWCNT paper electrodes the chemical stage proceeds with the participation of the $[\text{Pyr}_1\text{Me}_3\text{COH}]^+\text{ads}$ radical cation adsorbed on the surface of SWCNT and MWCNT paper electrodes. Since the concentration of the catalytically active $\text{Pyr}_1^*\text{Me}_3\text{COH}^*\text{CNT}$ complex will dominate on the CNT surface, the contribution of the competing chemical reaction with MeCN will be negligible small.

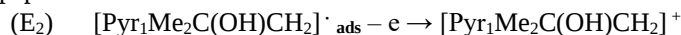


E₂—second electrode stage.

At GC electrode. At the second electrode stage, the radical intermediates are oxidized to the cations.

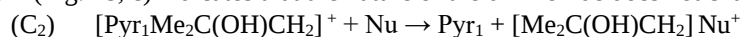


At SWCNT and MWCNT paper electrodes. The radical intermediate adsorbed on the surface of SWCNT and MWCNT paper electrodes is oxidized to the cation.

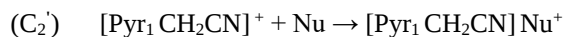


C₂—second chemical stage.

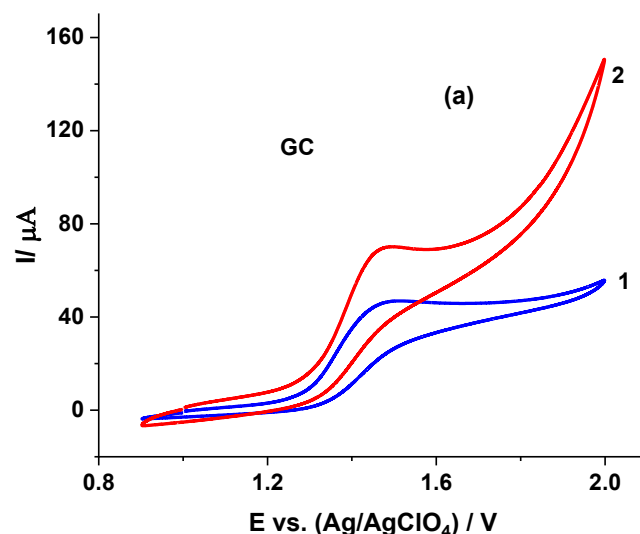
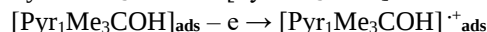
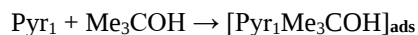
At GC, SWCNT and MWCNT paper electrodes. At the second chemical stage, the cations react with a nucleophile or a base (an admixture of water in solution) to form the initial aromatic di-N-oxide and the product of the two-electron oxidation Me_3COH . Registration of the EPR spectra of Pyr_1 radical cation and anion in tert-BuOH (Fig. 4b, c) indicates that the nature of the di-N-oxide does not change during the catalytic process.



At GC electrode. In a competitive chemical stage (C_2'), cation is attached to a base or nucleophile to form an adduct.



At SWCNT and MWCNT paper electrodes surface the regenerated aromatic di-N-oxide forms a complex $[\text{Pyr}_1\text{Me}_3\text{COH}]_{\text{ads}}$ which is further oxidized to a radical cation $[\text{Pyr}_1\text{Me}_3\text{COH}]^+\text{ads}$. The cycle is repeated, and the catalytic current of total two-electron oxidation of Me_3COH is recorded.



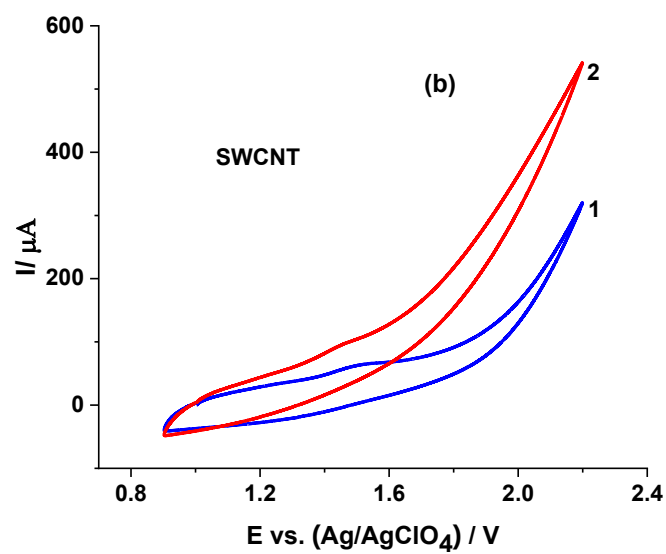
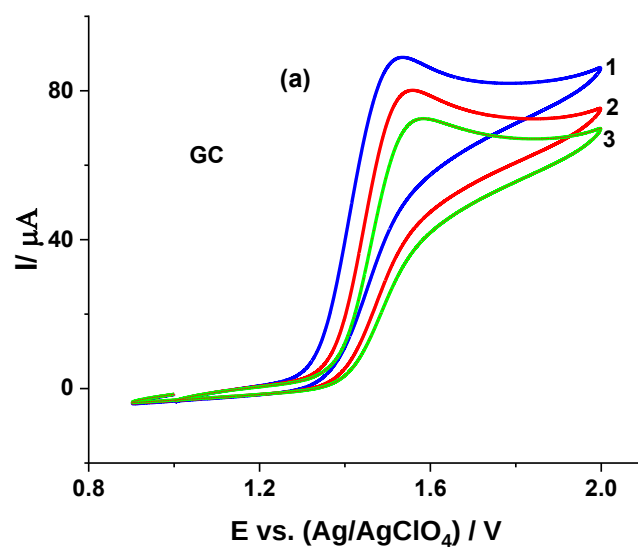


Figure 7. CVs of 0.5 mM Pyr₁ and 0.5 M tert-BuOH in 0.1 M Bu₄NClO₄ solution in MeCN at the potential scan rate of 20 mV/s in the presence of H₂O: (1) 0, (2) 2.0 M; (a) (GC) (b) SWCNT paper electrode



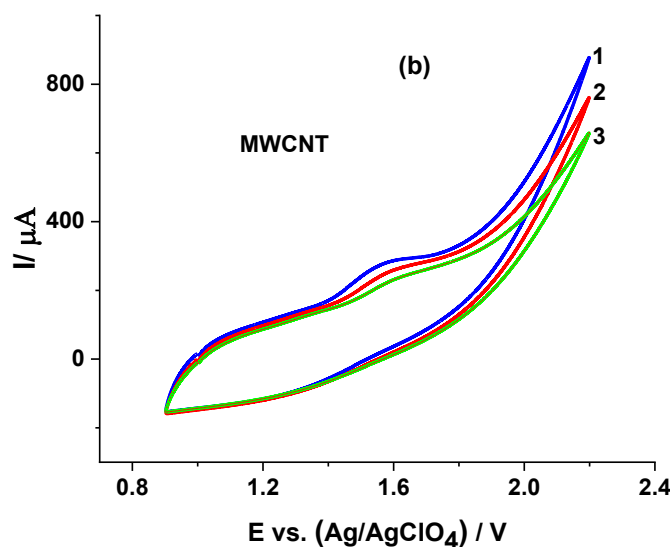


Figure 8. CVs of 1.0 mM Pyr₁ and 1.0 M tert-BuOH in 0.1 M Bu₄NClO₄ solution at the potential scan rate of 20 mV/s in MeCN in the presence of CH₃COOH: (1) 0, (2) 1.0, (3) 2.0 M; (a) (GC), (b) MWCNT paper electrode

4. Conclusions

In this work, the oxidation of Pyr₁ in 0.1 M of Bu₄NClO₄ in MeCN in the presence of tert-BuOH at SWCNT and MWCNT paper electrodes compared to the GC electrode was studied by the methods of cyclic voltammetry, quantum chemical modeling and EPR electrolysis. The energies of non-covalent interactions between the components of the Pyr₁-tert-BuOH-CNT electrocatalytic system in 0.1 M Bu₄NClO₄ in MeCN and the energies of their adsorption on the CNT surface were calculated using a cluster model describing the surface of conducting carbon nanotubes (10, 10).

It follows from the study that Pyr₁*Me₃COH*CNT complexes adsorbed on the positively charged surface of CNTs electrodes participate in the catalytic oxidation of tert-BuOH in 0.1 M Bu₄NClO₄ solution in MeCN. Since the adsorption energy of the Pyr₁*Me₃COH*CNT complex exceeds the adsorption energy of the Pyr₁*MeCN*CNT and MeCN*CNT complexes, the concentration of the catalytically active Pyr₁*Me₃COH*CNT complex will prevail on the CNT surface. Adsorption of the complex of di-N-oxide with tert-BuOH leads to an increase in the concentration of catalytically active species on the surface of CNTs electrodes compared to the GC electrode. As a result, the catalytic efficiency of the process on CNTs electrodes will exceed the catalytic efficiency of the process on the GC electrode.

The concentrations of the Pyr₁*MeCN*CNT and MeCN*CNT complexes will be negligible and, consequently, the occurrence of a competing chemical reaction of the Pyr₁ radical cation with MeCN on the CNT electrodes will be unlikely. These factors lead to an increase in the catalytic efficiency of the process at CNTs electrodes compared to GC electrode.

The study showed that the use of CNTs electrodes in electrocatalytic processes makes it possible to increase the catalytic efficiency of the oxidation of organic compounds, including those with a high activation energy of the C-H bond, in the presence of electrochemically generated radical cations of aromatic di-N-oxides by several times compared to the GC electrode. It was found, that the non-covalent functionalization of CNTs electrodes by catalytically active complexes is of decisive importance. This work will be useful at using CNTs electrodes in electrocatalytic processes as well as the aromatic di-N-oxide-CNTs catalytic systems in electrocatalysis and sensors.

Acknowledgments

This work was performed in accordance with the state task, state registration No AAAA-A19-119061890019-5. Calculations were performed at the Computer Center of Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry, RAS.

Conflict of interest

There is no conflict of interest for this study.

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