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Comparative Electrochemical and Electron Paramagnetic Resonance Study of the Mechanism of Oxidation of 2,3,5,6-Tetra-Me-Pyrazine-Di-N-Oxide as a Mediator of Electrocatalytic Oxidation of Methanol at Glassy Carbon and Multi-Walled Carbon Nanotube Paper Electrodes

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ABSTRACT

The comparative study of the mechanism of oxidation of 2,3,5,6-tetra-Me-pyrazine-di-N-oxide (Pyr_2) as a mediator of electrocatalytic oxidation of methanol (MeOH) was carried out at glassy carbon (GC) and multi-walled carbon nanotube (MWCNT) paper electrodes in 0.1 M $LiClO_4$ solutions in acetonitrile by the methods of cyclic voltammetry, EPR electrolysis, the dependence of the differential double layer capacitance of the electrode C on potential E, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). It was found that the oxidation current of Pyr_2 at MWCNT paper electrode (as in the case of SWCNT paper electrode found early) in the absence of MeOH exceeds by several times the oxidation current of the ferrocene reference. This effect is attributed to the adsorption of Pyr_2 at the surface of these electrodes and the subsequent increase in the surface concentration of Pyr_2 and the current of its oxidation. Catalytic currents were recorded during the oxidation of Pyr_2 at GC and MWCNT paper electrodes in presence of MeOH. The effect of MeOH, acid and water on the shape of CVs and the intensity of EPR signal of Pyr_2 radical cation was investigated. These results were explained by the $E_1C_1E_2C_2$ mechanism of two-stage electrode process characterized by catalytic current recorded at the second electrode stage. The overall two-electron catalytic oxidation of methanol in complex with the Pyr_2 radical cation was assumed to occur. The catalytic efficiency of MeOH oxidation increases by 7 times at the use of MWCNT paper electrode instead of GC. The results pointed out that in process of electrocatalytic oxidation organic compounds in the presence of aromatic di-N-oxides as mediators the effect of the electrodes made of SWCNT paper (studied earlier) and MWCNT paper (studied in this paper) are similar.

1. Introduction

The electrochemically generated aromatic di-N-oxide radical cations are carriers of active oxygen that is capable of activating the C-H bond of substrates: alcohols, ethers and cyclohexane [1-9]. The mechanism of the oxidation of phenazine-di-N-oxide (PhenDNO), pyrazine-di-N-oxide (PyrDNO), and its substituted derivatives as mediators of electrocatalytic oxidation alcohols, ethers, and cyclohexane was studied by cyclic voltammetry at glass carbon electrode in acetonitrile [1-9]. In the study of the oxidation of PhenDNO in methanol and its deuterated derivatives CH_3OD and CD_3OD by EPR electrolysis [3], EPR spectra of radical intermediates were recorded with g-factor of 2.0023 in CH_3OH and CH_3OD and 2.0023 and 2.0036 in CD_3OD. It was assumed that the radical intermediates were complexes of radical cation $PhenDNO^{+\bullet}$ with methanol and its deuterated derivatives. The detection of the same intermediate in CH_3OH and CH_3OD indicated that CH_3 group of alcohol was involved in formation of the intermediate. To explain the results obtained in [1-9], the $E_1C_1E_2C_2$ mechanism of two-stage electrode process characterized by catalytic current at the second electrode stage was suggested. The overall two-electron catalytic oxidation of the organic substance in complex with aromatic di-N-oxide radical cation was assumed to occur.

Carbon nanomaterials, single-walled (SWCNT) and multi-walled (MWCNT) nanotubes, nanopaper, nanofibers, have been extensively studied as a promising material for fundamental research [10-23], technological applications [24–33] (electronic materials and sensors) and electrocatalysis [34–46] due to their unique structural and physical properties: high surface area, excellent electronic conductivity, high chemical stability, and a wide useful potential window. Therefore, it was reasonable to study the possibility of using such electrodes in the processes of electrocatalytic oxidation of organic compounds in the presence of electrochemically generated aromatic di-N-oxide radical cation. We studied the mechanism of oxidation of PhenDNO in the presence of cyclohexanol [47] and PhenDNO and Pyr_2 in the presence isopropyl alcohol (i-PrOH) [48, 49] by the methods of cyclic voltammetry, EPR electrolysis and the differential capacitance at GC and SWCNT paper (produced in our institute [47] and produced by “NanoLab’s” firm (USA) [48, 49]) electrodes in 0.1 M $LiClO_4$ solutions in acetonitrile. It was found that the catalytic efficiency of oxidation of organic compounds at SWCNT electrodes in the presence of aromatic di-N-oxide increases several times as compared with oxidation at GC electrode.

In the present work the mechanism of oxidation of Pyr_2 in the presence of methanol was studied at GC electrode and for the first time at MWCNT paper electrode in 0.1 M $LiClO_4$ solutions in acetonitrile by the methods of cyclic voltammetry and the dependence of the differential double layer capacitance of the electrode C on potential E. The effect of MeOH, acid and water on the shape of CVs and the intensity of EPR signal of Pyr_2 radical cation was investigated.

2. Experimental Methods

The CVs were recorded at MWCNT paper and GC electrodes using an IPC-compact potentiostat (Moscow, Russia). A three-electrode cell was used for electrochemical measurements. 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 $LiClO_4$ solution in acetonitrile. The accuracy of potential recording was ±0.01 V. Before the experiment, GC electrode was polished with micron sandpaper. Then GC electrode was kept for 5 min in acetone and further washed by tridistilled water and dried. MWCNT paper electrode was washed by acetone and tridistilled water and dried. Before recording of CV in 0.1 M $LiClO_4$ solution in

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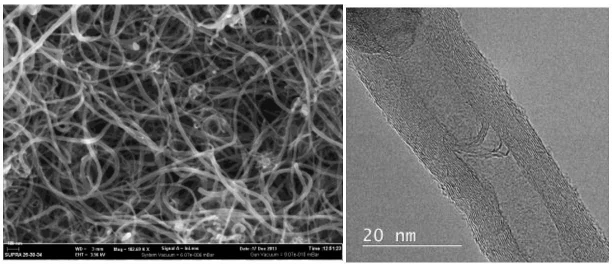
acetonitrile, the electrodes were polarized doubly for 10 s at 1.0 and 1.5 V and then CVs were recorded in the potential range of 1.0 to 2.2 V. Before recording of each CV in investigation solution, the electrodes were polarized for 40 s at 1.0 V. The visible surface of GC was 0.181 cm^2. Before the experiments, oxygen dissolved in solution was removed by bubbling of argon (high purity grade) through the cell. During experiments, the argon flow over solution preventing the penetration of oxygen to solution.

Electrodes from carbon nanopaper were obtained as described in a previously studied work [50]. The characteristic size of this working nanopaper electrode was 2 × 4 mm. Nanopaper 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) (Fig. 1a and b) nanopaper contains multi-walled carbon nanotubes with diameter of ~20 nm and length of ~2 μm. Transmission electron micrographs were obtained with FEI Technai Osiris transmission electron microscope operating at 200 kV. Samples for transmission electron microscopy were predispersed in acetone by ultrasonication in an ultrasonic bath for 50 min. Then the suspension was pipetted onto a copper TEM grid with microholed amorphous carbon substrate and set up to dry in air.



(a) (b)

Fig. 1 (a) Scanning microscopy image of MWCNT paper electrode; (b) high-resolution electron microscopy (HREM) image of a fragment of MWCNT with various number of cylindrical graphene layers in walls (18-22)

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 by Ioffe et al. [51]. A helix of platinum or gold wire ~0.31 mm in diameter served as a working electrode, a cylinder of Pt foil was an auxiliary electrode, and a 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.

The dependence of the differential capacitance C of MWCNT paper electrode on potential E was measured by a potentiostat – galvanostat Autolab /FRA (Netherlands) at 370 Hz and the ac voltage amplitude of 1 mV. The potential of working electrode relative to saturated calomel electrode was varied by steps of 50 mV with detention for 3 s at each E. The C vs E curves were recorded in regions 0-1.8 V in 0.1 M $LiClO_4$ solution in acetonitrile, 0-1.4 V in the presence of 1 mM Pyr$_2$ (at these potentials Pyr$_2$ is neither oxidized nor reduced) and in 0–1.2 V region in the presence of 1 mM Pyr$_2$ and 0.5 M MeOH after recording CV curve in corresponding regions at the potential scan rate 20 mV/s.

Acetonitrile and methanol of HPLC grade were used. $LiClO_4$ was purified by double recrystallization from solution in tridistilled water with subsequent drying at low pressure and temperatures which do not exceed 200 °C. The experimental procedure of the Pyr$_2$ synthesis was described in details in [52]. The 0.1 M $LiClO_4$ solution in acetonitrile was used as a supporting electrolyte in all experiments.

3. Results and Discussion

3.1 Oxidation of Pyr$_2$ at GC and MWCNT Paper Electrodes in Acetonitrile

The oxidation of Pyr$_2$ at GC electrode by the method of cyclic voltammetry was studied early [49] in 0.1M $LiClO_4$ solution in acetonitrile. It was found that the current of anodic peak of Pyr$_2$ oxidation (1.4 V) is proportional to square root of the scan rate and concentration of Pyr$_2$ indicating the diffusion character of the electrochemical process. The process is irreversible and corresponds to EC process when the charge transfer is followed by irreversible chemical reaction. The rate of chemical reaction of radical cation Pyr$_2^{+\bullet}$ with acetonitrile molecule 0.54 s^{-1} was estimated by Kulakovskaya et al. [49] from the ratio of currents of cathodic to anodic peak as described in some studies [53, 54]. At electrolysis at Pt electrode in 0.1 M $LiClO_4$ solution in acetonitrile [49] was recorded the EPR spectrum of radical cation of Pyr$_2$ at positive potential at decreasing temperature down to -45 ^{o}C. Parameters of EPR spectrum of Pyr$_2$: g-factor = 2.0089, Gaussian line of 1.45 mT width between extreme. The intensity of the EPR signal reached its maximum at 1.6 V and does not changed at further increasing the potential up to 2.4 V. This indicated that this radical cation is not further oxidized to a dication in this range of E.

The potential of oxidation of Pyr$_2$ (1.7 V) at MWCNT paper electrode (Fig. 2a), is higher as compared by oxidation at GC electrode. The process is irreversible and not diffusion-controlled because the difference between potentials of the anodic and cathodic peaks is 100 mV and the oxidation current of Pyr$_2$ does not increase directly proportional to the square root of potential scan rate (Fig. 2b) and concentration of Pyr$_2$ from 0.5 up to 1.0 mM (Fig. 2c). The oxidation current of Pyr$_2$ (Fig. 2d) exceeds by several times the diffusion current of oxidation of 1 mM ferrocene (as a reference current, we used the diffusion current of ferrocene oxidation which proceeds reversibly with the loss of one electron). These features of Pyr$_2$ oxidation at MWCNT paper electrode are similar observed at SWCNT paper electrode [49] and correspond to the compounds adsorbed at the surface of electrode [55]. The shift of potential of Pyr$_2$ oxidation at MWCNT paper electrode may be explained by necessity of overcoming adsorption forces at discharge of adsorbed particles.

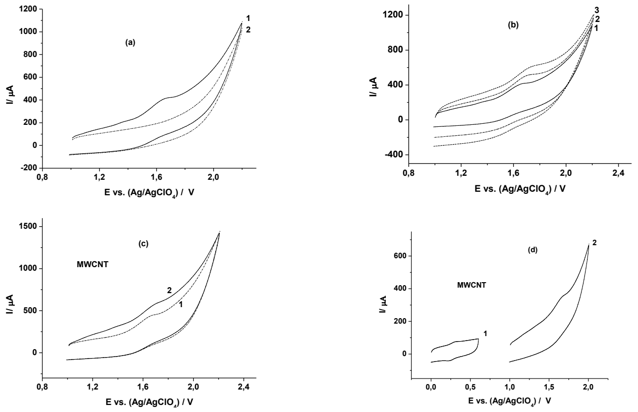


Fig. 2 CVs of the 0.1 M $LiClO_4$ solution in acetonitrile at MWCNT paper electrode in the presence of (a) (1) 1.0, (2) 0 mM Pyr$_2$ at a potential scan rate of 20 mV/s; (b) 1 mM Pyr$_2$ at potential scan rates of (1) 20, (2) 50, (3) 80 mV/s; (c) (1) 0.5, (2) 1.0 mM Pyr$_2$ at a potential scan rate of 20 mV/s; (d) (1) 1 mM ferrocene and (2) 1 mM Pyr$_2$ at a potential scan rate of 20 mV/s

To support that adsorption of Pyr$_2$ at MWCNT paper electrode in investigated systems takes place the measurements of C,E- dependences for the first time were carried out (Fig. 3). It was found that in the presence of 1 mM Pyr$_2$ the capacity of MWCNT paper electrode is decreased. It is in agreement with Lazer et al. reports [56], where it was shown that at graphene-like materials carbocycles with conjugated π-bonds possess higher adsorbability as compared with acetonitrile. The addition of 0.5 M MeOH to 1 mM Pyr$_2$ results in further decrease of the double layer capacity. This testifies adsorption of MeOH on the surface of MWCNT paper electrode and formation of a mixed layer which includes molecules both Pyr$_2$ and MeOH.

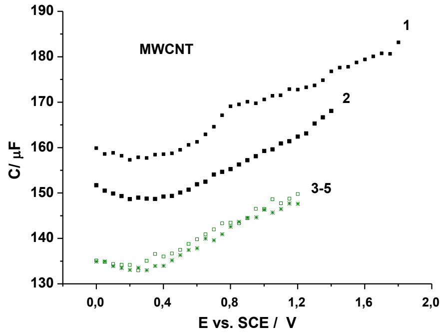


Fig. 3 Dependences of the differential capacitance C of MWCNT paper electrode on potential E of the 0.1 M $LiClO_4$ solution in acetonitrile in the presence of Pyr$_2$: 0 (curve 1) and 1 mM (curve 2), 1 mM Pyr$_2$ and 0.5 M i-PrOH (curve 3-5). Curves 1 and 2 were recorded just after recording cyclic voltammetry curves, curves 3, 4 and 5 are settled curves

Earlier [47, 48] we found that the oxidation current of PhenDNO at SWCNT paper electrode exceeded by several times the oxidation current of ferrocene reference. To clarify the mechanism of this effect, we performed [47] a quantum-chemical modeling of adsorption of PhenDNO

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and ferrocene at CNT electrode. We found that the estimated adsorption energy of PhenDNO on nanotube was by 8.0 kJ/mol higher than that of ferrocene. The increase in the interaction energy for PhenDNO can be attributed to the increase in the donor–acceptor component of interaction. If we assume that the change in the entropy of the system during the formation of the adsorption complexes of PhenDNO and ferrocene with the surface of CNT electrode is approximately the same in the two cases, the concentration of PhenDNO on the surface is ≈ 30 times higher than that of ferrocene at low values of surface coverage.

As in the case of PhenDNO oxidation [47, 48], the increase of the current of Pyr_2 oxidation at SWCNT [49] and MWCNT paper electrodes (found in this work) by several times as compared with that for ferrocene can be explained by Pyr_2 adsorption which results in the increase of Pyr_2 concentration on the electrode surface and, as a consequence, in the increase of its oxidation current.

3.2 Oxidation of Pyr_2 at GC and MWCNT Paper Electrodes

The CV curves obtained at GC electrode in 0.1 M $LiClO_4$ solution in acetonitrile in the presence of MeOH (Fig. 4a) show that the oxidation of MeOH in the given range of potentials is not observed in the absence of Pyr_2. A second anodic peak appears at higher anodic potentials at CV of Pyr_2 oxidation at GC electrode in 0.1 M $LiClO_4$ solution in acetonitrile after adding 0.05 M MeOH to the solution (Fig. 4b). At increasing MeOH concentration from 0.01 up to 0.1 M the current of first anodic peak increases unsubstantially and its potential shifts to lower positive values whereas the current of the second anodic peak increases (Fig. 4c), and the start of the increase of the anodic current shifts to the first anodic peak. At the concentration of MeOH 0.1 M and higher the first and second anodic peaks are merged. Simultaneously the cathodic peak of the reduction of the Pyr_2 radical cation to Pyr_2 decreases gradually and disappears at 0.05 M MeOH (Fig. 4d). The disappearance of the cathodic peak indicates the interaction of the radical cation with MeOH.

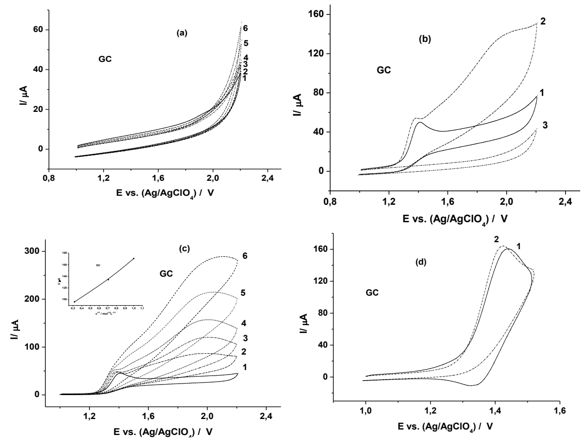

Fig. 4 CVs of the 0.1 M $LiClO_4$ solution in acetonitrile at GC electrode at a potential scan rate of 20 mV/s in the presence MeOH: (a) (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5, (6) 1.0 M; (b) (1) 1 mM Pyr_2, (2) 1 mM Pyr2 and 0.05 M MeOH, (3) 0.05 M MeOH; (c) 1 mM Pyr_2 and MeOH: (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5, (6) 1.0 M; (inset of c dependence of the anodic peak current on the square root of the MeOH concentration); (d) (1) 1 mM Pyr_2, (2) 1 mM Pyr_2 and 0.05 M MeOH at potential scan rate of 200 mV/s

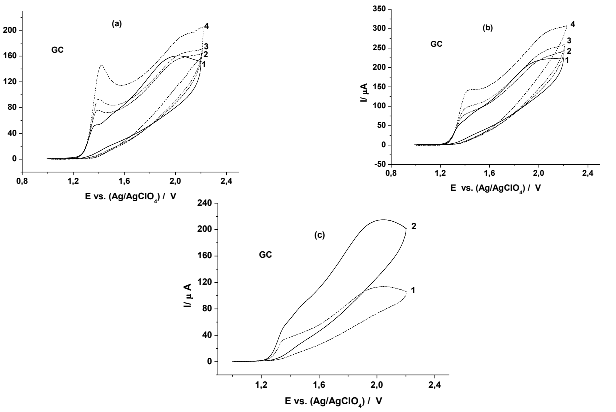

Fig. 5 CVs of the 0.1 M $LiClO_4$ solution in acetonitrile at GC electrode in the presence: (a) of 1 mM Pyr_2 and 0.1 M MeOH at potential scan rate: (1) 20, (2) 50, (3) 80, (4) 200 mV/s; (b) 1 mM Pyr_2 and 0.5 M MeOH at potential scan rate: (1) 20, (2) 50, (3) 80, (4) 200 mV/s; (c) 0.5 M MeOH and Pyr_2: (1) 0.5 mM, (2) 1 mM at a potential scan rate of 20 mV/s

To determine the mechanism of oxidation of Pyr_2 in the presence of MeOH we studied the dependence of anodic peaks on the scan rate. It was found that at MeOH concentration between 0.01 and 0.5 M the current of first anodic peak increases proportionally to square root of the scan rate (Fig. 5a) indicating the diffusion character of the electrochemical process. The second anodic peak is irreversible and decreases with the increase of the potential scan rate at MeOH concentrations lower 0.5 M (Fig. 5a). This means that this peak is of kinetic nature and $E_1C_1E_2$ mechanism is realized when two stages of electron transfer are separated by a chemical stage C_1 [53, 54].

At the concentration of MeOH higher 0.05 M, the current of the second anodic peak is proportional to square root of the concentration of MeOH (inset, Fig. 4c) and at 0.5 M MeOH the current of the anodic peak weakly depends on the potential scan rate (Fig. 5b) and is proportional to the concentration of Pyr2 (Fig. 5c). According to Galus et al. [55], these data testifies the catalytic nature of the second anodic peak. Catalytic efficiency of the process α (the ratio of the catalytic oxidation current of Pyr_2 in the presence of 0.5 M MeOH to the current recorded in the absence of MeOH at the same GC electrode) was 4.0 True value of catalytic efficiency should be higher because a competitive reaction of radical cation of Pyr_2 with solvents decreases this value. The existence of this competitive reaction is revealed by irreversibility of Pyr_2 oxidation and the appearance of EPR spectrum of radical cation only at lowering temperature down to –45 °C.

Note that in the presence of MeOH in acetonitrile solutions, no EPR spectrum of radical cation of Pyr_2 could be detected. The EPR spectrum of radical cation of Pyr_2 was detected in [7] at electrolysis at Au electrode only at temperature close to the solvent freezing point at -90° C when deuterated derivatives of methanol (CH_3OD and CD_3OD) were used as a solvent and substrate simultaneously (Fig. 6b and c). Parameters of EPR spectrum of radical cation Pyr_2: g-factor = 2.0089, Gaussian line of 1.45 mT width between extreme. The direct observation of EPR spectrum of radical cation of Pyr_2 in solutions of deuterated methanol derivatives suggest that Pyr_2 structure remains unchanged during the alcohol catalytic oxidation.

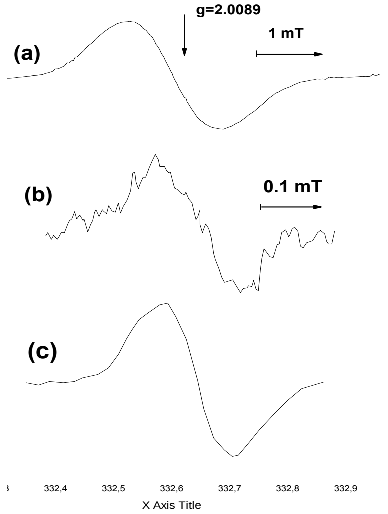

Fig. 6 EPR spectra of a radical cation (a, b, c) of Pyr_2 recorded at the electrolysis of the 0.1 M $LiClO_4$ solution in different solvents in the presence of 1 mM Pyr_2 at different temperatures and potentials: (a) in acetonitrile at –45 °C and +1.6 V, (b) in CH_3OD at –90 °C and +1.6 V, (c) in CD_3OD at –90 °C and +1.35 V. Spectrum (a) was obtained at Pt electrode, the other spectra were obtained at Au electrode

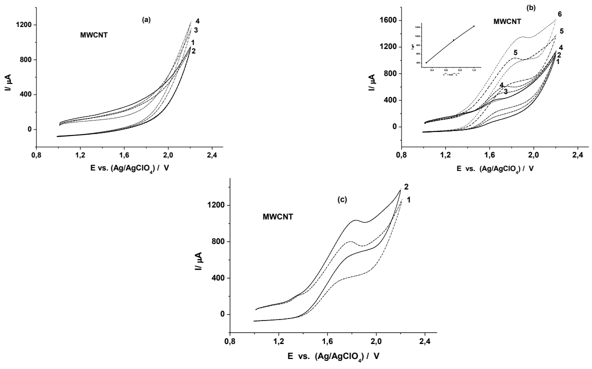

Fig. 7 CVs of the 0.1 M $LiClO_4$ solution in acetonitrile at MWCNT paper electrode at a potential scan rate of 20 mV/s in the presence MeOH: (a) (1) 0.01, (2) 0.05, (3) 0.5, (4) 1.0 M; (b) (1) 1 mM Pyr_2 and MeOH: (1) 0, (2) 0.01, (3) 0.05, (4) 0.1, (5) 0.5, (6) 1.0 M; (inset of b dependence of the anodic peak current on the square root of the MeOH concentration); (c) 0.5 M MeOH and Pyr_2: (1) 0.5, (2) 1.0 mM

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As in the case of GC electrode the CV curves obtained at MWCNT paper electrode in 0.1 M $LiClO_4$ solution in acetonitrile in the presence of MeOH (Fig. 7a) show that the oxidation of MeOH in the given range of potentials is not observed in the absence of Pyr_2.`At the addition of MeOH to acetonitrile solution of 0.1 M $LiClO_4$ the oxidation current of Pyr_2 at MWCNT paper electrode increases and the start of the increase of the anodic current shifts to lower positive potentials on the CVs (Fig. 7b) as in the case of GC electrode.

According to Galus et al. [55], the linear dependence of the maximum of the anodic peak of Pyr_2 oxidation on the square root of the concentration of MeOH (inset, Fig. 7b) suggests the catalytic nature of the observed anodic current. The catalytic efficiency of the process α (per ferrocene as reference) is 27 at 0.5 M MeOH. Thus, the use of MWCNT paper electrode increases the catalytic efficiency of MeOH oxidation by ~7 times.

The catalytic current increases with the increase of Pyr_2 concentration (Fig. 7c). However, in contrast to the GC electrode, on which I_a increases in proportion to the concentration of Pyr_2 (Fig. 5c), at the MWCNT paper electrode I_a increases only factor 1.3. This is probably because we record the already increased oxidation current of Pyr_2.

To elucidate mechanism of electrode process, we studied the effect of addition of CH_3COOH and water (as a base) on the potential of catalytic wave and catalytic current of Pyr_2 oxidation at GC and MWCNT paper electrodes in the presence of MeOH. Addition of 1.0 and 2.0 M of CH_3COOH to solution containing 0.5 mM of Pyr_2 and 0.5 M of MeOH results in the decrease of catalytic current and the shift of catalytic wave to higher positive potentials (Fig. 8a and b). The addition of H_2O results in the increase of catalytic current and the shift of catalytic wave at GC electrode to potentials of anodic wave of Pyr_2 oxidation (Fig. 8c). The catalytic current of the oxidation of Pyr_2 increases by 1.9 times at the addition of 2.0 M H_2O. In the case of MWCNT paper electrode the addition of H_2O shifts the catalytic wave to lower positive potentials (Fig. 8d). However the shift is less than that in the case of GC electrode. The shift of catalytic waves at GC and MWCNT paper electrodes to lower positive potentials after addition of H_2O shows that the potential of oxidation of a product of interaction of Pyr_2 radical cation with MeOH is close to potential of Pyr_2 oxidation.

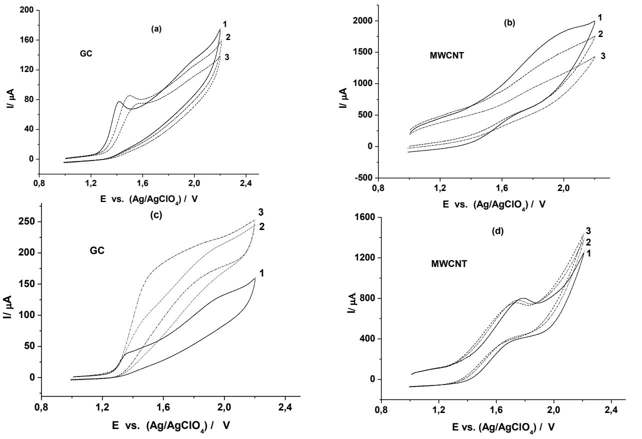
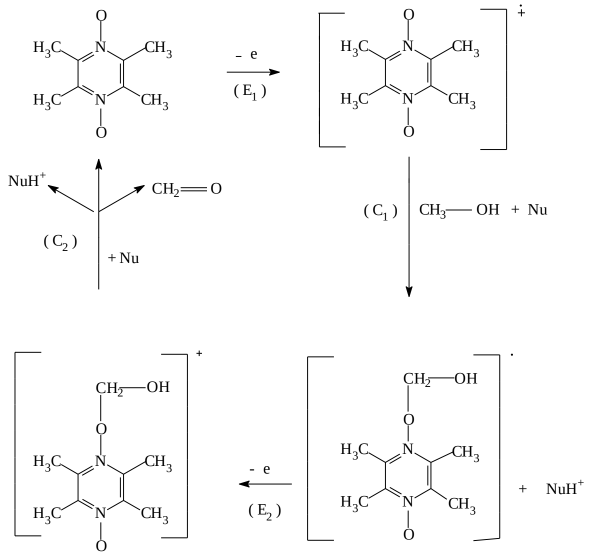


Fig. 8 CVs of 0.5 mM Pyr_2 and 0.5 M MeOH in the 0.1 M $LiClO_4$ solution in acetonitrile in the presence CH_3COOH: (1) 0, (2) 1.0, (3) 2.0 M; (a) (GC) and (b) (MWCNT paper) electrodes at the potential scan rate of 50 mV/s; and H_2O: (c) (GC) (1) 0, (2) 1.0, (3) 2.0 M; (d) (MWCNT paper) (1) 0, (2) 0.5, (3) 1.0 M at the potential scan rate of 20 mV/s

The effect of addition of CH_3COOH and water (as a base) on the potential of catalytic wave and catalytic current of Pyr_2 oxidation at GC and MWCNT paper electrodes in the presence of MeOH show that the catalytic process is accompanied by proton elimination. Similar effect of addition of CH_3COOH and of H_2O on catalytic oxidation of PhenDNO and Pyr_2 in the presence of i-PrOH at GC and SWCNT paper electrodes observed earlier studies [48, 49]. Based on the obtained experimental data, the oxidation of Pyr_2 in the presence of MeOH at the GC electrode can be explained by the $E_1C_1E_2C_2$ mechanism proposed earlier [1–9] for the two-stage electrode process characterized by the catalytic current recorded at the second electrode stage.

At the first electrode stage (E_1) in Scheme 1, aromatic di-N-oxide is oxidized to the radical cation. The electrophilic addition of the oxygen atom of the radical cation to the C-H bond of organic substance occurs at the first chemical stage (C_1). The reaction is accompanied by proton elimination and the formation of a radical intermediate (a complex with an N-O-C structure). Compounds of this structure and methods for their preparation are known [57-63]. At the second electrode stage (E_2), the radical intermediate is oxidized to the cation.



Scheme 1 Mechanism of 2,3,5,6-tetra-Me-pyrazine-di-N-oxide oxidation in the presence of MeOH

The next chemical stage (C_2) corresponds to the interaction of the cation with a nucleophile or base (a water admixture in the solution). Since there are catalytic currents in the presence of organic substance, we assumed that the cation decomposes at the C_2 stage to form the starting aromatic di-N-oxide and the product of the two-electron oxidation of organic substance. The regenerated aromatic di-N-oxide is immediately oxidized to the radical cation and the cycle is repeated, and the catalytic current of the total two-electron oxidation of the substrate is recorded. The oxidation of Pyr_2 at the MWCNT paper electrode in the presence of MeOH can be explained by the above-considered mechanism. The difference of the shapes of CVs at GC and MWCNT paper electrodes may be due to different adsorbability of Pyr_2 on these electrodes.

4. Conclusion

The comparative study of the mechanism of oxidation of 2,3,5,6-tetra-Me-pyrazine-di-N-oxide (Pyr_2) as a mediator of electrocatalytic oxidation of methanol (MeOH) was carried out at glassy carbon (GC) and multi-walled carbon nanotube (MWCNT) paper electrodes in 0.1 M $LiClO_4$ solutions in acetonitrile by the methods of cyclic voltammetry, EPR electrolysis, the dependence of the differential double layer capacitance of the electrode C on potential E, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HR-TEM). It was found that the oxidation current of Pyr_2 at MWCNT paper electrode (as in the case of SWCNT paper electrode found early) in the absence of MeOH exceeds by several times the oxidation current of the ferrocene reference. This effect is attributed to the adsorption of Pyr_2 at the surface of these electrodes and the subsequent increase in the surface concentration of Pyr_2 and the current of its oxidation. Catalytic currents were recorded during the oxidation of Pyr_2 at GC and MWCNT paper electrodes in presence of MeOH. The effect of MeOH, acid and water on the shape of CVs and the intensity of EPR signal of Pyr_2 radical cation was investigated. These results were explained by the $E_1C_1E_2C_2$ mechanism of two-stage electrode pr**oc**ess characterized by catalytic current recorded at the second electrode stage. The overall two-electron catalytic oxidation of methanol in complex with the Pyr_2 radical cation was assumed to occur. The catalytic efficiency of MeOH oxidation increases by 7 times at the use of MWCNT paper electrode instead of GC. The results pointed out that in process of electrocatalytic oxidation organic compounds in the presence of aromatic di-N-oxides as mediators the effect of the electrodes made of SWCNT paper (studied early) and MWCNT paper (studied in this paper) are similar.

References

[1] S.I. Kulakovskaya, V.M. Berdnikov, A.Y. Tikhonov, L.B. Volodarskii, V.E. Maier, A cyclic voltammetric study of the mechanism responsible for the oxidation of organic compounds on a glass-carbon electrode in the presence of aromatic N,N′-dioxides as organic mediators, Russ. J. Electrochem. 29 (1993) 40-45.

[2] S.I. Kulakovskaya, V.M. Berdnikov, A.A. Vasilenko, A.Y. Tikhonov, L.B. Volodarskii, The mechanism of electrochemical activation of the C-H bond

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during oxidation of organic compounds in the presence of aromatic N-oxides as the intermediates, Russ. J. Electrochem. 32 (1996) 784-790.

[3] S.I. Kulakovskaya, A.V. Kulikov, V.M. Berdnikov, N.T. Ioffe, A.F. Shestakov, Electrochemical and EPR study of the C-H bond activation, Electrocatalytic oxidation with participation of radical cation of phenazine-di-N-oxide, Electrochim. Acta 47 (2002) 4245-4254.

[4] S.I. Kulakovskaya, A.V. Kulikov, A.F. Shestakov, Radical cation of pyrazine-di-N-oxide as a mediator in electrocatalytic oxidation of organic compounds, Russ. J. Electrochem. 40 (2004) 1035-1044.

[5] S.I. Kulakovskaya, A.V. Kulikov, A.F. Shestakov, Substituted pyrazine-di-N-oxydes as the mediators of catalytic oxidation of organic compounds, Russ. J. Electrochem. 43 (2007) 1156 - 1163.

[6] S.I. Kulakovskaya, A.V. Kulikov, A.F. Shestakov, Electrochemical and EPR-study of the mechanism of organic compound oxidation in the presence of mediators – radical cations of substituted pyrazine-di-N-oxydes, Russ. J. Electrochem. 43 (2007) 1234-1242.

[7] S.I. Kulakovskaya, A.V. Kulikov, A.F. Shestakov, Electrochemical and EPR studies of the oxidation mechanism of pyrazine-di-N-oxides in the presence of methanol and its deuterated derivatives, Russ. J. Electrochem. 48 (2012) 1023-1036.

[8] S.I. Kulakovskaya, A.V. Kulikov, A.F. Shestakov, Electrochemical and EPR studies of tert-butanol oxidation mechanism in the presence of radical cations of pyrazine-di-N-oxide and its substituted derivatives as mediators, Russ. J. Electrochem. 46 (2010) 1047-1055.

[9] S.I. Kulakovskaya, A.V. Kulikov, A.F. Shestakov, Electrochemical and EPR studies of the methane C-H bond activation in the presence of radical cations of pyrazine-di-N-oxide and its substituted derivatives, Russ. J. Electrochem. 45 (2009) 1368-1375.

[10] M. Pumera, The electrochemistry of carbon nanotubes: fundamentals and application, Chem. Eur. J. 15 (2009) 4970-4978.

[11] M. Pumera, T. Sasaki, H. Iwai, Relationship between carbon nanotube structure and electrochemical behavior: heterogeneous electron transfer at electrochemically activated carbon nanotubes, Chem. Asian. J. 3 (2008) 2046-2055.

[12] A.G. Krivenko, N.S. Komarova, Electrochemistry of nanostructured carbon, Russ. Chem. Rev. 77 (2008) 995-1012.

[13] I. Streeter, G.G. Wildgoose, L. Shao, R.G. Compton, Cyclic voltammetry on electrode surfaces covered with porous layers: an analysis of electron transfer kinetics at single-walled carbon nanotube modified electrodes, Sens. Actuat. B 133 (2008) 462-466.

[14] C.E. Banks, X. Ji, A. Crossley, R.G. Compton, Understanding the electrochemical reactivity of bamboo multi-walled carbon nanotubes: the presence of oxygenated species at tube ends may not increase electron transfer kinetics, Electroanal. 18 (2006) 2137-2140.

[15] I. Heller, J. Kong, K.A. Williams, C. Dekker, S.G. Lemay, Electrochemistry at single-walled carbon nanotubes: the role of band structure and quantum capacitance, J. Am. Chem. Soc. 128 (2006) 7353-7359.

[16] P. Szroeder, Electron transfer kinetics at single-walled carbon nanotube paper: the role of band structure, Physica E 44 (2011) 470-475.

[17] A.G. Guell, N. Ebejer, M.E. Snowden, J.V. Macpherson, P.R. Unwin, Structural correlations in heterogeneous electron transfer at monolayer and multilayer grapheme electrodes, J. Am. Chem. Soc. 134 (2012) 7258-7261.

[18] J.N. Barisci, G.G. Wallace, R.H. Baughman, Electrochemical characterization of single-walled carbon nanotube electrodes, J. Electrochem. Soc. 147 (2000) 4580-4583.

[19] M.M. Rahman, I.C. Jeon, Studies of electrochemical behavior of SWCNT-film electrodes, J. Braz. Chem. Soc. 18 (2007) 1150-1157.

[20] E.J.E. Stuart, M. Pumera, Impurities within carbon nanotubes govern the electrochemical oxidation of substituted hydrozines, Phys. Chem. Chem. Phys. 13 (2011) 10818-10822.

[21] A. Ambrosi, M. Pumera, Amorphos carbon impurities play an active role in redox processes of carbon nanotubes, J. Phys. Chem. C 115 (2011) 25281-25284.

[22] A. Heras, A. Colina, J. Lopez-Palacios, P. Ayala, J. Sainio, V. Ruiz, E. I. Kauppinen, Electrochemical purification of carbon nanotube electrodes, Electrochem. Commun.11 (2009) 1535-1538.

[23] I. Kruusenberg, N. Alexeyeva, K. Tammeveski, J. Kozlova, L. Matisin, V. Sammelselg, et al., Effect of purification of carbon nanotubes on their electrocatalytic properties for oxygen reduction in acid solution, Carbon 49 (2011) 4031-4039.

[24] S. Zhu, G. Xu, Single-walled carbon nanohorns and their applications, Nanoscale 2 (2010) 2538-2549.

[25] K. Gong, S. Chakrabarti, L. Dai, Electrochemistry at carbon nanotube electrodes: is the nanotube tip more active than the sidewall?, Angew. Chem. Int. Ed. 47 (2008) 5446-5450.

[26] K. Balasubramanian, M. Burghard, K. Kern, Effect of the electronic structure of carbon nanotubes on the selectivity of electrochemical functionalization, Phys. Chem. Chem. Phys. 10 (2008) 2256-2262.

[27] K. Balasubramanian, T. Kurkina, A. Ahmad, M. Burghard, K. Kern, Tuning the functional interface of carbon nanotubes by electrochemistry: Toward nanoscale chemical sensors and biosensors, J. Mat. Res. 27 (2012) 391-402.

[28] J.E. Weber, S. Pillai, M.K. Ram, A. Kumar, S.R. Singh, Electrochemical impedance-based DNA sensor using a modified single walled carbon nanotube electrode, Mater. Sci. Eng. C 31 (2011) 821-825.

[29] J. Shen, A. Liu, Y. Tu, G. Foo, C. Yeo, M.B. Chan-Park, R. Jiang, Y. Chen, How carboxylic groups improve the performance of single-walled carbon nanotube electrochemical capacitors, Energy Environ. Sci. 4 (2011) 4220-4229.

[30] L. Yan, X. Niu, Z. Wen, Xiaoyan Li, Xiaobao Li, W. Sun, Application of single-walled carbon nanohorn modified electrode for the direct electrochemistry of myoglobin, J. Electrochem. Sci. 11 (2016) 8972-8980.

[31] Y. Fan, C. Han, B. Zhang, Recent advances in the development and application of nanoelectrodes, Analyst 141 (2016) 5474-5487.

[32] M. Noked, A. Soffer, D. Aurbach, The electrochemistry of activated carbonaceous materials: past, present, and future, J. Solid State Electrochem. 15 (2011) 1563-1578.

[33] H. Bi, Y. Li, S. Liu, P. Guo, Z. Wei, C. Lv, J. Zhang, X.S. Zhao, Carbon-nanotube-modified glassy carbon electrode for simultaneous determination of dopamine, ascorbic acid and uric acid: The effect of functional groups, Sens. Actuat. B 171-172 (2012) 1132-1140.

[34] J. Zhu, A. Holmen, D. Chen, Carbon nanomaterials in catalysis: proton affinity, chemical and electronic properties, and their catalytic consequences, Chem. Cat. Chem. 5 (2013) 378-401.

[35] J. Wu, Y. Xue, X. Yan, W. Yan, Q. Cheng, Y. Xie, Co_3O_4 nanocrystals on single-walled carbon nanotubes as a highly efficient oxygen-evolving catalyst, Nano Res. 5(8) (2012) 521-530.

[36] K. Gong, F. Du, Z. Xia, M. Durstock, L. Dai, Nitrogen-doped carbon nanotube arrays with high electrocatalytic activity for oxygen reduction, Sci. 323 (2009) 760-764.

[37] S. Wang, D. Yu, L. Dai, Polyelectrolyte functionalized carbon nanotubes as efficient metal-free electrocatalysts for oxygen reduction, J. Am. Chem. Soc. 133 (2011) 5182-5185.

[38] W. Lv, K. Shi, L. Li, S. Shao, Nitrogen-doped multi-walled carbon nanotubes and their electrocatalysis towards oxidation of NO, Microchim. Acta 170 (2010) 91-98.

[39] P. Canete-Rosales, V. Ortega, A. Alvarez-Lueje, S. Bollo, M. Gonzalez, A. Anson, M.T. Martinez, Influence of size and oxidative treatments of multi-walled carbon nanotubes on their electrocatalytic properties, Electrochim. Acta 62 (2012) 163-171.

[40] T. Ramulifho, K.I. Ozoemena, R.M. Modibedi, C.J. Jafta, M.K. Mathe, Electocatalytic oxidation of ethylene glycol at palladium-bimetallic nanocatalysts (PdSn and PdNi) supported on sulfonate-functionalised multy-walled carbon nanotubes, J. Electroanal. Chem. 692 (2013) 26-30.

[41] R. Cao, R. Thapa, H. Kim, X. Xu, M.G. Kim, Q. Li, et al., Promotion of oxygen reduction by a bio-inspired tethered iron phthalocyanine carbon nanotube-based catalyst, Nat. Commun. 4 (2013) 2076-1-7.

[42] D. Zhou, L. Ding, H. Cui, H. An, J. Zhai, Q. Li, Fabrication of Pd/TiO_2-multiwall carbon nanotubes catalyst and investigation of its electrocatalytic activity for formic acid oxidation, J. Power Sources 222 (2013) 510-517.

[43] Y. Gan, H. Huang, W. Zhang, Electrocatalytic oxidation of methanol on carbon-nanotubes/graphite electrode modified with platinum and molybdenum oxide nanopaticles, Trans. Nonferrous Met. Soc. China 17 (2007) 214-219.

[44] S. Wang, X. Wang, S.P. Jiang, PtRu Nanoparticles supported on 1-aminopyrene functionalized multi-walled carbon nanotubes and their electrocatalytic activity for methanol oxidation, Langmuir 24 (2008) 10505-10512.

[45] Y. Zhao, X. Yang, J. Tian, F. Wang, L. Zhan, Methanol electro-oxidation on Ni@Pd core-shell nanoparticles supported on multi-walled carbon nanotubes in alkaline media, Int. J. Hydr. Energy 35 (2010) 3249 -3257.

[46] H. An, L. Pan, H. Cui, D. Zhou, B. Wang, J. Zhai, et al., Electrocatalytic performance of Pd nanoparticles supported on TiO_2-MWCNTs for methanol, ethanol, and isopropanol in alkaline media, J. Electroanalyt. Chem. 741 (2015) 56-63.

[47] S.I. Kulakovskaya, A.G. Krivenko, N.S. Komarova, A.V. Kulikov, A.F. Shestakov, Electrochemical and EPR study of the mechanism of oxidation of phenazine-di-N-oxide in the presence of cyclohexanol on glass carbon and single-walled carbon nanotube electrodes, Russ. J. Electrochem. 50 (2014) 1-12.

[48] S.I. Kulakovskaya, A.V. Kulikov, L.N. Sviridova, E.V. Stenina, Electrochemical and electron paramagnetic resonance study of the mechanism of oxidation of phenazine-di-N-oxide in the presence of isopropyl alcohol at glassy carbon and single-walled carbon nanotube electrodes, Electrochim. Acta 146 (2014) 798-808.

[49] S.I. Kulakovskaya, A.V. Kulikov, L.N. Sviridova, E.V. Stenina, Electrochemical and electron paramagnetic resonance study of the mechanism of oxidation of 2,3,5,6-tetra-Me-pyrazine-di-N-oxide as a mediator of electrocatalytic oxidation of isopropyl alcohol at glassy carbon and single-walled carbon nanotube electrodes, J. Electroanal. Chem. 795 (2017) 81-89.

[50] A.G. Krivenko, V.I. Matyushenko, E.V. Stenina, L.N. Sviridova, A.V. Krestinin, G.I. Zvereva, et al., Peculiarities of the electrochemical behavior of modified electrodes containing single-wall carbon nanotubes, Electrochem. Comm. 7 (2005) 199-204.

[51] N.T.Ioffe, V.G. Mairanovskii, The cell for the study of reaction kinetics of electron exchange by method of EPR-electrolysis, Elektrokhimiya 22 (1986) 1695-1697.

[52] L.H. Grigoryeva, A.Y. Tikhonov, S.A. Amitina, L.B. Volodarskii, I.K. Korobeinicheva, Interaction of 1,2-hydroxylamineoximes with 1,2-diketones, Conversion of 2-acyl-1-hydroxy-3-imidazoline-3-oxides into pyrazine-1,4-dioxides, Chem. Heterocyc. Comp. N 3 (1986) 331-338.

[53] R.S. Nicholson, J. Shain, Theory of stationary electrode polarography, Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems, Anal. Chem. 36 (1964) 706-723.

[54] R.S. Nicholson, J. Shain, Theory of stationary electrode polarography for a chemical reaction coupled between two charge transfers, Anal. Chem. 37 (1965) 178-189.

[55] Z. Galus, Fundamentals of electrochemical analysis, Harwoood, New York, 1976.

[56] P. Lazar, F. Karlicky, P. Jurecka, M. Kocman, E. Otyepkova, K. Safarova, M. Otyepka, Adsorption of small organic molecules on graphene, J. Am. Chem. Soc. 135 (2013) 6372-6377.

[57] V.A. Golubev, R.V. Miklyush, E.G. Rozantsev, Method of synthesis of ketoether of N-oxypiperidine, Russ. Chem. Bull. 3 (1972) 656-658.

[58] V.A. Golubev, R.V. Miklyush, New preparative method of the oxydation of methylene group to carbonyl, Russ. J. Org. Chem. 8 (1972) 1356-1357.

https://doi.org/10.30799/jaec.053.18040103

Cite this Article as: S.I. Kulakovskaya, A.V. Kulikov, L.N. Sviridova, E.V. Stenina, A.G. Ryabenko, V.G. Basu, Comparative electrochemical and electron paramagnetic resonance study of the mechanism of oxidation of 2,3,5,6-tetra-Me-pyrazine-di-N-oxide as a mediator of electrocatalytic oxidation of methanol at glassy carbon and multi-walled carbon nanotube paper electrodes, J. Adv. Electrochem. 4(1) (2018) 162–167.

[59] A.R. Katritzky, The preparation of some substituted pyridine 1-oxides, J. Chem. Soc. 70 (1956) 2404-2408.
[60] T. Okamoto, H. Tani, Synthesis of 2- and 4-cyanopyridincs, Chem. Pharm. Bull. 7 (1959) 130-131.
[61] T. Okamoto, H. Tani, Reaction mechanism in aromatic heterocyclic compound. The reactions of N-alkoxypyridinium derivatives, Chem. Pharm. Bull. 7 (1959) 925-930.
[62] A.R. Katritzky, E. Lunt, N-oxides and related compounds-XXXV, Reactions of N-alkoxy-pyridinium and quinolinium cations with nucleophiles, Tetrahedron 25 (1969) 4291-4305.
[63] R. Eisenthal, A.R. Katritzky, The ring-opening of N-methoxypyridinium perchlorate by hydroxide ion, Tetrahedron 21 (1965) 2205-2213.

https://doi.org/10.30799/jaec.053.18040103

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