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Oxidation and Homolytic Coupling Regioselectivity of Carbazole in Acidic Media

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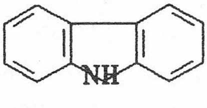
Using voltammetric technique with a rotating disk electrode, the anodic oxidation of carbazole in aqueous H_2SO_4 – ethanol mixtures was shown to proceed under diffusion and electron transfer control conditions. Electro-oxidation involves one electron transfer; electrode passivation occurs due to the formation of a poorly soluble product. By means of the SCF MO LCAO INDO, AM1-UHF and PM3-UHF methods, oxidative coupling regioselectivity for carbazole has been elucidated. Chemical oxidation of carbazole by ammonium vanadate in sulphuric acid medium features the stoichiometry 1 : 2, first order in substrate and first order in oxidant, and leads to the occurrence of the diimine dication of carbazole.

INTRODUCTION

The data on electro-oxidation of carbazole (**I**) and its derivatives in acetonitrile,$^{1-6}$ acetonitrile – water,^{7} methanol,^{5} dimethyl sulphoxide^{8} on platinum,$^{1-6,\,8}$ carbon, PbO_2-electrodes^{5} and transparent electrode in vacuum^{7} have been reported. The corresponding anodic reactions lead to the formation of



I

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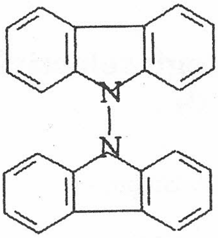
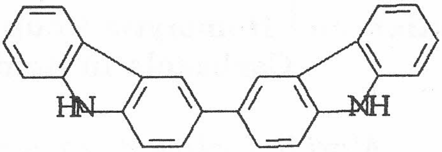
cation radicals,[2–4] aminyl radicals,[8] carbazoles dimers – 9,9'-(**II**), 3,3'-dicarbazyls (**III**) and their derivatives,[1,3–5] the cation radicals and diimine dications of (**III**) and the corresponding substituted species,[1,3,4] as well as polymer films.[6,7]


II


III

By means of oxidation of (**I**) and its *N*-ethyl and *N*-phenyl derivatives on gold, platinum and carbon electrodes in the presence of 1.25 M $HClO_4$ in aqueous – methanol (3 : 1) solution, conducting polymer films have been obtained. It has been proposed that the films are the result of formation of C-C bonds between the initial monomers.[9] The study of carbazole (**I**) electro-oxidation in acidic media on rotating disk electrode is of interest.

Chemical oxidation of dibenzpyrrole (**I**) was also dealt with. Treatment of (**I**) with potassium permanganate in acetone, silver oxide[10,11] or nickel peroxide in diethyl ether[12] yields (**II**). However, interaction of (**I**) with $KMnO_4$ or $K_2Cr_2O_7$ in acetic acid medium,[11] as well as with $Pb(CH_3COO)_4$[13] in acidic solution, leads to (**III**). The reaction of (**I**) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and tri(*p*-bromophenyl)amine cation radical salts shows an analogous result.[14] When heating 9-substituted carbazoles with palladium(II) acetate, 9,9'-disubstituted 3,3'-dicarbazyls occur.[15] In the reaction of (**I**) and *N*-ethylcarbazole with nitrosonium tetrafluoroborate, the cation radicals of the corresponding 3,3'-dimers appear.[16] The 9-methylcarbazole nitration by nitric acid is featured by the 3,3'-dimer formation; further interaction with HNO_3, probably, allows to obtain a dimeric cation radical.[17,18]

Thus, both the chemical and electrochemical oxidation of carbazoles proceeds *via* the occurrence of radical intermediates. In the cases when the steric factor hinders the dimerization, stable aminyl and nitroxyl radicals, as well as cation radicals derived from (**I**) form.[19]

A mechanistic interpretation of carbazole (**I**) chemical and electrochemical oxidations, especially in acidic solutions, needs further development.

The aim of the present work is voltammetric and spectrophotometric investigation of carbazole (**I**) oxidation in acidic media, along with a quantum chemical study of homolytic oxidative coupling regioselectivity of (**I**).

EXPERIMENTAL

Voltammetry

A glassy carbon rotating disk working electrode of standard construction (devised by the Design Office of A. N. Frumkin Institute of Electrochemistry, U. S. S. R. Academy of Sciences) with a surface area of 0.035 cm^2 was used together with a spiral platinum wire as an auxiliary electrode and a saturated Ag/AgCl electrode (KCl, w = 0.2647) as a reference electrode. The working electrode was polished with fine-grained »zero« type emery paper at the angular velocity ω = 209.4 rad/s, and subsequently washed with water. In general, ω was in the range of 81.7–303.7 rad/s. Current-potential curves were recorded in the potential sweep mode with a P-5848 potentiostat (manufactured by the Measuring Instruments Plant, Gomel, U. S. S. R.); the current was recorded using a LKD-4 recorder (manufactured by the same Plant). The potential sweep rate was 4 mV/s. The initial potential was 0.2 V, and the final one 1.5 V.

Chronoamperometry

In order to determine the number of electrons involved in the redox process, the method of Hitchman and Albery[20] was applied. Current decay curves were collected by registration of current values at constant potential 1.10 V *vs.* saturated Ag/AgCl electrode during 25 minutes after potential application. For registration of decay curves, another glassy carbon disk electrode with a surface area of 0.636 cm^2 was used.

Semiempirical Calculations

Quantum chemical calculation by the SCF MO LCAO method with the INDO[21] approximation was carried out using the VIKING package[22] program on a BESM-6 electronic computer (manufactured by the Account-Analytical Machines Plant, Moscow, U. S. S. R.).

The AM1[23] and PM3[24] calculations within the UHF formalism[22,25–27] were performed using the MOPAC package[27,28] software on an IBM PC AT-586 (Pentium) computer.

UV/VIS Spectroscopy

Electronic spectra were obtained using a Specord M40 spectrophotometer. Kinetic measurements were carried out with a KFK-2 photoelectric colorimeter using a colour filter No. 8 (λ_{max} = 670 nm).

RESULTS AND DISCUSSION

The literature data[1–18] analysis suggests that in our case (acidic media) the following oxidation mechanism for carbazole (**I**) should be expected:

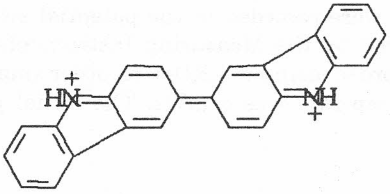
$$\mathrm{I} \rightleftharpoons \text{Cation radical of } \mathbf{I} + e^-, \tag{1}$$

$$2 \text{ Cation radical of } \mathbf{I} \longrightarrow \mathbf{III} + 2H^+. \tag{2}$$

Probably, further oxidation of (**III**) may occur:

$$\mathbf{III} \rightleftharpoons \mathbf{IV} + 2e^-, \tag{3}$$

forming diimine dication (**IV**):



IV

We have obtained current-voltage curves of anodic oxidation of 1 mM carbazole (**I**) in solutions of sulphuric acid containing ethanol, $\phi = 50\%$, and 0.3 M LiCl as supporting electrolyte (Figure 1).

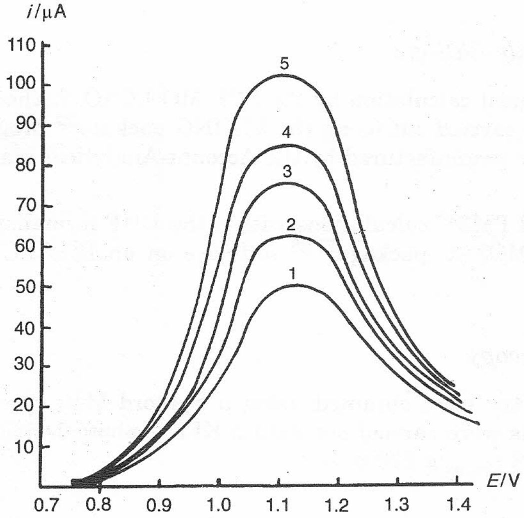


Figure 1. Voltammograms of anodic oxidation of 1 mM carbazole solutions in 5.25 M H_2SO_4 + ethanol (1 : 1) mixtures and 0.3 M LiCl as supporting electrolyte at different angular velocity of the disk electrode:
(1) 81.7, (2) 117.3, (3) 167.6, (4) 209.4, (5) 303.7 rad/s; sweep rate 4 mV/s. Potential values *vs.* saturated Ag/AgCl reference electrode are presented.

The absence of competing electrochemical processes is confirmed by the fact that the background current did not exceed 3–5% of the overall current. The possibility of the reaction

$$H_2SO_4 + LiCl \longrightarrow LiHSO_4 + HCl$$

proceeding was excluded by the medium components mixing conditions. Namely, sulphuric acid solutions were added to aqueous solutions of LiCl, whereas the reaction above proceeds while adding concentrated H_2SO_4 to dry lithium chloride. Even if the interaction between sulphuric acid and lithium chloride occured, it would not interfere with the anodic process studied, because carbazole (**I**) and its oxidation product (**III**) under the experimental conditions neither participate in acid-base equilibria (see below) nor interact with the reactants and the resulting compounds. If the reaction between H_2SO_4 and LiCl took place, it would not effect the state of the cation radical of (**I**) – oxidation intermediate because the acid excess is conserved. Lithium sulphate is unfit for a supporting electrolyte, being poorly soluble in ethanol and water – ethanol mixtures.

The curves have one peak with a maximum. No regular alterations in $E_{\max}$ with varying angular velocity can be observed. The maximal current has a diffusion nature which is displayed by a linear dependence of $i_{\max}$ on $\omega^{1/2}$.

For a heterogeneous first order electrode reaction, which is controlled by both the diffusion and electron transfer kinetics, equation[29] is valid:

$$i^{-1} = A + B\omega^{-1/2},$$
$$A = 1/nFkC^*, \quad B = 1.61\nu^{1/6}/nFD^{2/3}C^*,$$

where

n – the number of electrons involved in the anodic process,
k – the reaction rate constant,
C^* – the bulk concentration of depolarizer,
ν – the kinematic viscosity,
D – the diffusion coefficient.

The character of the whole current-voltage curve indicates the diffusion and electron transfer control conditions[29] of the electro-oxidation. It is confirmed by the linear dependence of i^{-1} on $\omega^{-1/2}$ at the potentials 0.94, 0.98, 1.00, 1.08, 1.10, 1.14, 1.16, 1.20, 1.24 V (Figure 2, Table I).

The dependence mentioned made it possible to estimate the first-order rate constants (Table I), assuming $n = 1$ (see below). The values obtained diminish when the potential increases (from 1.10 V), while the contrary is expected. This is due to the fact that the electron transfer rate constants were calculated in a potential domain where electrode pollution occurs.

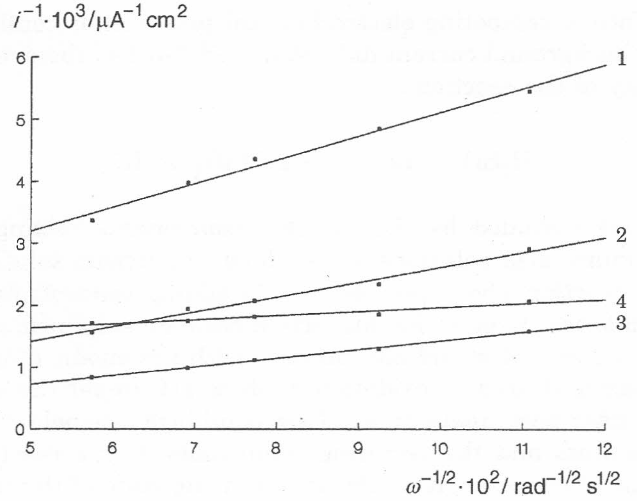


Figure 2. Plots presenting $i^{-1}/\mu A^{-1}$ cm^2 *vs.* $\omega^{-1/2}/rad^{-1/2}$ s$^{1/2}$ at different potentials (E/V *vs.* saturated Ag/AgCl reference electrode): (1) 0.94, (2) 0.98, (3) 1.08, (4) 1.24.

TABLE I

Dependence of i^{-1} / μA^{-1} cm^2 on $\omega^{-1/2}$ / rad$^{-1/2}$ s$^{1/2}$ (confidence probability $P = 0.95$) $i^{-1} = A + B\omega^{-1/2}$

Potential / V	$B \times 10^2$ / $\mu A^{-1} cm^2 rad^{1/2} s^{-1/2}$	$A \times 10^4$ / $\mu A^{-1} cm^2$	k × 10^3 / cm s^{-1}
0.94	3.84 ± 0.272	12.8 ± 2.27	8.08
1.10	1.24 ± 0.0793	1.37 ± 0.662	75.5
1.14	1.14 ± 0.0522	3.04 ± 0.436	34.1
1.16	1.14 ± 0.0350	3.79 ± 0.292	27.4
1.20	0.852 ± 0.0584	8.57 ± 0.488	12.1
1.24	0.668 ± 0.112	13.0 ± 0.937	7.95

The maximal potential value for dibenzpyrrole (**I**) anodic oxidation within the range of sulphuric acid concentrations studied, *i.e.* 4.25 to 7.85 mol/l, exhibits no acidity dependence. It indicates that electro-oxidation is not complicated by protolytic equilibria, and the species predominating in the bulk of solution is transported to electrode. Analysis of the data on carbazole (**I**) basicity ($pK_b \approx 20^{30-35}$) provides an evidence that, under the experimental conditions, substance (**I**) exists mainly in an unprotonated molecular form, which is oxidized. 3,3'-Dicarbazyl (**III**) is also not protonated under the aforesaid conditions. The only media for the compound (**I**), and obviously also (**III**) to be protonated involve 96% H_2SO_4 or 70% $HClO_4$.[36]

Total current of the reaction under diffusion and electron transfer control conditions depends on potential E as follows:[37]

$$i = i_0 \{\frac{C_{\mathrm{OS}}}{C_{\mathrm{O}}{}^*} \exp [-\alpha nF (E-E_e) / RT] -$$

$$- \frac{C_{\mathrm{RS}}}{C_{\mathrm{R}}{}^*} \exp [(1-\alpha) nF (E-E_e) / RT]\},$$

where

i_0 – the exchange current,

C_{OS} and C_{RS} – the concentrations of oxidized and reduced forms near the surface of electrode,

$C_{\mathrm{O}}{}^*$ and $C_{\mathrm{R}}{}^*$ – the corresponding bulk concentrations,

α – the electrochemical transfer coefficient,

E_e – the equilibrium potential.

Beyond E_e, one of partial currents (the current of reduction, for the given case) could be neglected, and linear dependence of ln i on E should be expected:

$$\ln i = G + HE,$$

$$G = \ln (i_0 C_{\mathrm{OS}} / C_{\mathrm{O}}{}^*) + \alpha nFE_e / RT, \quad H = -\alpha nF / RT$$

From the above dependence for diffusion and electron transfer controlled potential domain 1.10 to 1.24 V, using the kinetic current values (1/A from the connection between i^{-1} and $\omega^{-1/2}$), we have determined the value of $\alpha n = 0.41$ ($G = 26.7 \pm 3.90$; $H = -16.3 \pm 3.34$; $P = 0.95$; i in μA cm^{-2}, E in V).

Considering the value of $\alpha \approx 0.5$ for the majority of electrochemical reactions,[37] a one-electron character of carbazole (**I**) oxidation should be assumed.

The maximal current decay curves at the potential 1.10 V in aqueous sulphuric acid (with concentrations 5.25 and 7.25 mol/l) – ethanol mixtures have been investigated (Figure 3). At the initial stage of the process, high gradient of concentration appears at the electrode surface; the flow of substance transferred by diffusion is great as compared to the convective flow, and the next condition is valid:[29, 37]

$$i = nFDC^*(\pi Dt)^{-1/2}.$$

With time t, the diffusion and convective flows become comparable with each other, and steady extreme flow is set. Therefore, a linear relationship between $i_{\max}$ and $t^{-1/2}$ observed for the initial parts of the curves indicates a stationary diffusion regime still unestablished.

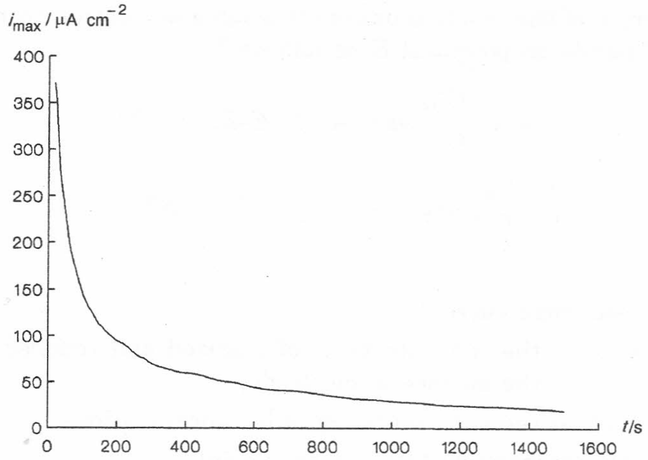


Figure 3. The maximal current decay curve at potential 1.10 V *vs.* saturated Ag/AgCl reference electrode in 5.25 M aqueous sulphuric acid – ethanol mixtures.

Thus, within the initial period 108 s of the decay curve collection for carbazole (**I**) oxidation in the mixture 7.85 M H_2SO_4 + ethanol, the parameters of the corresponding straight line are as follows:

$$i_{max} = M + Nt^{-1/2},$$
$$M = -429 \pm 37.1, \quad N = 6091 \pm 734$$

(11 points considered; $P = 0.95$; the dimensions: i_{max}/μA cm^{-2}, t/s, M/μA cm^{-2}, N/μA cm^{-2} s$^{1/2}$).

Using the method of Hitchman and Albery,[20] the diffusion coefficient of the electro-active substance was found: 2.06 × 10^{-4} cm^2 s^{-1} in the mixture of ethanol and 5.25 M sulphuric acid; 4.83 × 10^{-4} cm^2 s^{-1} in the mixture of ethanol and 7.85 M H_2SO_4. The values of n obtained from the analysis of decay curves are low and fractional, which together with a decrease in the slope of the line $i^{-1} = f(\omega^{-1/2})$,[29] observed for increasing potentials (0.94–1.24 V) (Figure 2, Table I), provides an evidence for a nonsteady state behaviour of the electrode surface due to its passivation as a result of the electrode reaction. This phenomenon may be related to precipitation of the poorly soluble dimer or polymer of carbazole (**I**) onto the electrode surface. Thus, within the aforesaid kinetics, the current is controlled by electron transfer and diffusion limitations, as well as influenced by the decrease of the electrode free area.

Current-voltage curves analogous to those obtained in our case, with a diffusion current at maximum and platinum electrode passivation at rather positive potentials, under diffusion and electron transfer kinetics conditions were reported for the ionization of molecular hydrogen.[29] A linear dependence between anodic current and $\omega^{1/2}$ is known for the process of iron electrode inhibition in a phosphate solution;[38] the corresponding voltammograms have maxima in a number of cases.[39]

The structure of the product of oxidative dimerization (and also polymerization) of (**I**) is of interest. As reported, in anodic processes of (**I**) in various media, (**II**) and (**III**)[1, 3–5, 10–18] or polymer films based on the aforementioned compounds[6,7] occur.

In our case of one-electron oxidation accompanied by electrode passivation, also only a dimer or polymer is to be the reaction product, since monomeric species do not precipitate onto the electrode surface.

In order to describe the dimerization step of oxidation, we have calculated the spin density distribution on the atoms of the cation radical of carbazole (**I**) using the INDO, AM1-UHF and PM3-UHF schemes.

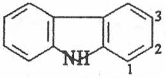
The INDO method is favourably parameterized for reproducing spin density values on atoms of molecular systems with open electronic shells.[22, 23] Geometry parameters of the initial molecule[40–42] were used for the cation radical of carbazole (**I**). Correctness of such a consideration is confirmed by literary data.[43,44] Moreover, we have shown that the spin density distribution in the cation radical of diphenylamine and in diphenylaminyl radical does not essentially depend upon the geometry assumed – is it either »standard« or optimized.[45]

The AM1-UHF and PM3-UHF studies were carried out with complete geometry optimization (Broyden – Fletcher – Goldfarb – Shanno function minimizer)[46, 47] involving Thiel's fast minimization routine.[47] The preliminary optimization was realized by the MMX method[48] with the PCMODEL package[48] software on an IBM PC AT-586 (Pentium) computer. In quantum chemical calculations, the gradient norm did not exceed 0.06 and 0.02 (kcal/mol)/Å for the AM1 and PM3 methods, respectively.

In Table II, one can observe spin densities in different positions of the carbazole (**I**) cation radical. According to the INDO data, as well as the re-

TABLE II

Spin densities on atoms in the cation radical of carbazole



Calculation method	1	2	3	4	N
	Position of molecular system				
INDO	0.174	–0.100	0.164	–0.051	0.733
AM1	0.445	–0.376	0.438	–0.242	0.713
PM3	0.415	–0.356	0.402	–0.241	0.782

sults obtained by means of more sophisticated approaches AM1-UHF and PM3-UHF, an excess of spin density occurs on the nitrogen atom and, to a lesser extent, on the carbon atoms in positions 1 and 3.

The steric factor, by analogy to the data[45] for diphenylamines, rejects the possibility of coupling with participation of position 1 of the molecule; the absence of 1,1'-, 1,3'- and 1,9'-dicarbazyls among the oxidation products of carbazole has been confirmed experimentally.[1, 3–5, 10–18] We have shown[45] that the homolytic (oxidative and reductive) coupling regioselectivities for organic compounds of various kinds are regulated by spin densities on atoms in the corresponding radical intermediates. As for the present paper, spin density accounts for a preferential formation of 9,9'-dicarbazyl (**II**) during carbazole (**I**) oxidation in media with sufficiently low acidity.[1, 3–5, 10–12] On the other hand, in acidic media the N-N bond appears to be labile,[49–51] and the recombination of the cation radicals of (**I**) *via* position 3 yields (**III**).

A confirmation of the validity of the approach to predicting the possibility and directions of homolytic coupling consists in the fact that phenothiazine, the cation radical of which shows lesser values of spin density (INDO) on atoms N (0.468), C-1 (0.029), C-3 (0.071) as compared to the cation radicals of (**I**) and diarylamines,[45] does not undergo oxidative dimerization under similar conditions.[52]

No direct (spectroelectrochemical, coulometric, preparative) evidence could be provided for the nature of the carbazole (**I**) oxidation product. The latter passivates the electrode surface and cannot be preparatively isolated or characterized *in situ*, unlike the dimers obtained by Ambrose *et al.*[1] which have been synthesized by chemical means and compared with the species formed electrochemically by matching of cyclic polarograms and visible absorption spectra.

To confirm indirectly the dimeric character and structure of the carbazole (**I**) oxidized form, we have performed chemical oxidation of (**I**) (from 2.0×10^{-5} to 3.2×10^{-4} mol/l) under conditions (ammonium vanadate, from 4.0×10^{-5} to 3.6×10^{-4} mol/l, as the oxidant, and 5.35 M H_2SO_4 as the medium) similar to those of electrochemical investigation. The $E^o = 0.802$ V value *vs.* saturated Ag/AgCl electrode at 298 K[53] for the process

$$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O \tag{4}$$

is close to the potentials from 0.9 to 1.4 V of the (**I**) electro-oxidation. Rather high acidity used in the present work allows the real potential of the semireaction (4) to grow as compared to E^o, and the closeness mentioned becomes more strongly pronounced. Moreover, water and aqueous – ethanol media are close to each other by solvating ability, since water and ethanol have similar donor and acceptor numbers, Dimroth and Reichardt solvent polarity parameters E_T, dipole moments of molecules, chemical properties due to the OH-groups existence.[54]

Spectrophotometric kinetic measurements using the method of Neues and Ostwald[55] have shown that the reaction has first order in substrate (**I**) and first order in oxidant. Spectral curves in the electronic absorption spectra of the oxidized form of carbazole (**I**) feature bands with λ_{max} = 401.9 and 735.3 nm. The latter are analogous to those registrated by Ambrose *et al.*[1] in acetonitrile (two bands at 382 and 760 nm, assigned to the cation radical and dication of (**III**), respectively), and to those observed for diarylamines in the case of complexation of *N,N'*-diaryl-*p*-diphenoquinonediimine dications (the products of diphenylamines oxidation) and diarylbenzidines or unoxidized amines.[56, 57] It should be mentioned that the oxidation forms of diphenylamines in acidic media have not yet been isolated due to their comparable instability.[56] By means of the isomolar series and molar ratios methods, the stoichiometry of (**I**) oxidation by NH_4VO_3 was shown to be 1 : 2. Thus, the chemical oxidation of (**I**) leads to the formation of the diimine dication (**IV**), which may occur only from dimer (**III**), but not (**II**), according to scheme (3).

In general, the results of the present work together with previous data[1, 3–5, 11, 13–19] confirm the mechanism of the carbazole (**I**) electro-oxidation, including the consecutive processes (1) and (2). Also polymerization of (**III**) may occur.[9]

Hereby, electro-oxidation of (**I**) on a glassy carbon rotating disk electrode in aqueous H_2SO_4 – ethanol mixtures represents a one-electron process, while chemical oxidation by vanadate in sulphuric acid solution involves two electrons, and the limiting step is bimolecular.

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SAŽETAK

Oksidacija i regioselektivnost homolitičkog sparivanja karbazola u kiselom mediju

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Voltammetrijom s rotirajućom disk-elektrodom utvrđeno je da brzinu anodne oksidacije karbazola u vodenim smjesama sumporne kiseline i etanola kontroliraju difuzija i prijenos elektrona. Elektrooksidacija uključuje prijenos jednog elektrona. Zbog nastajanja slabo topljivog produkta dolazi do pasivacije elektrode. Regioselektivnost oksidativnog sparivanja karbazola procijenjena je postupcima SCF MO LCAO INDO, AM1-UHF i PM3-UHF. Kemijska oksidacija karbazola amonijevim vanadatom u nazočnosti sumporne kiseline ima stehiometriju 1 : 2, prvog je reda s obzirom na supstrat i oksidans i rezultira nastajanjem diiminskog dikationa karbazola.