COULOMETRY IN RESONATOR CAVITY OF EPR SPECTROMETER: ELECTROCHEMICAL OXIDATION OF CARBAZOLE METHYL DERIVATIVES

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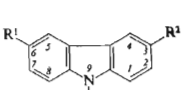
Electrochemical reduction of carbazole, 3-methyl- and 3,9-dimethylcarbazole in acetonitrile leads to the formation of a layer of conductive, insoluble products on the electrode surface of a partially radical character. This phenomenon was studied by coulometry in the resonator cavity of an EPR spectrometer with simultaneous measuring of the spin concentration. With carbazole and 3-methylcarbazole, the radical particles are formed with a yield of about 2% with respect to the current passed, whereas with 3,9-dimethylcarbazole this yield is by an order or magnitude lower. The radical product adsorbed on the electrode is probably a sparingly soluble perchlorate of the cation radical of 3,3′- or 6,6′-bicarbazole. 3,6,9-Trimethylcarbazole gives on oxidation a relatively stable primary cation radical. Electrochemical oxidation of 9-methyl- and 3,6-dimethylcarbazole does not lead to radical products.

Electrochemical oxidation of carbazole and its derivatives in acetonitrile on a platinum electrode was studied in detail by Ambrose and Nelson[1,2] with regard to a possible formation of cation radicals. They proved electrochemically and UV-spectroscopically that primarily formed cation radicals of carbazole and its N-substituted derivatives undergo a very rapid consecutive dimerization to 3,3′-bicarbazole or in the presence of proton acceptors to 9,9′-bicarbazole. The former is oxidized to a dication at the potential of the first oxidation peak of carbazole[1]. Ambrose and Nelson proved by the method of internal electrochemical generation of radicals that during the electro-oxidation of both unsubstituted carbazole and 3,3′-bicarbazole a simple EPR signal of the same form and width is obtained, which they, however, did not study in more detail[1]. Relatively stable cation radicals, which can be studied in solution by EPR spectroscopy, can be obtained only by electro-oxidation of 3,6,9--substituted carbazoles[2].

The aim of the present work is to elucidate quantitatively the formation of insoluble radical products of the oxidation of carbazole and some of its methyl derivatives as well as their composition. We used carbazole derivatives in which the most reactive positions of the cation radical are blocked with methyl groups in all possible combinations:



		R^1	R^2	R^3
I	carbazole	H	H	H
II	9-methylcarbazole	H	H	CH_3
III	3-methylcarbazole	CH_3	H	H
IV	3,9-dimethylcarbazole	CH_3	H	CH_3
V	3,6-dimethylcarbazole	CH_3	CH_3	H
VI	3,6,9-trimethylcarbazole	CH_3	CH_3	CH_3

EXPERIMENTAL

Chemicals

Carbazole of reagent grade (Lachema, Brno) was used; 9-methylcarbazole was synthesized from the former according to Ambrose and Nelson and its melting point was 91°C as given by them[1]. 3-Methylcarbazole was prepared by the Ullmann synthesis according to Borsch[3] from bromobenzene and 2-nitro-4-toluidine (synthesized according to Gattermann[4]); m.p. 209—210°C (ref.[3] gives 203°C); 3-9-dimethylcarbazole was synthesized from 3-methylcarbazole, prepared as given above, analogously to 9-methylcarbazole; m.p. 84°C (no data in the literature). 3,6-Dimethylcarbazole was prepared by the Ullmann synthesis according to Vaníček and Allan[5] from 4-bromotoluene (synthesized according to Gilman[6] from 4-toluidine) and 2-nitro-4-toluidine (synthesized according to Gattermann[4] from 4-toluidine); m.p. 218°C (ref.[5] gives 217—218°C). 3,6,9-Trimethylcarbazole was synthesized from 3,6-dimethylcarbazole, prepared as given above, analogously to 9-methylcarbazole; m.p. 121°C (no data in the literature). The purity of all the derivatives was checked by thin-layer chromatography (Silufol UV 254, Kavalier, ČSSR).

Cyclic Voltammetry and EPR Spectroscopy

The experimental conditions during studies with these methods, including internal electrochemical generation of radicals, calibration of the magnetic axis of the EPR spectrum, and measurement of the g factor, were the same as earlier[7].

Coulometry in Resonator Cavity of EPR Spectrometer

In this method, which was used to measure the current yield of the radical products, a platinum wire electrode was used (0·3 mm in diameter). The wire was sealed in glass except for its 5 mm end portion, which reached into the center of the electrolytic space in the resonator. The electrode was inserted into the cell for the electrochemical generation of radicals from above. The solution was 0·1M-$N(C_2H_5)_4ClO_4$ in nonaqueous acetonitrile containing 0·001M depolarizer. The EPR signal was recorded during electrolysis and measurement of the charge passed. The latter was corrected for the residual current, which was at the beginning of electrolysis equal to several

percent of the total current. On the assumption that the relative sensitivity changes in the resonator vertically as the square of the cosine function, the correction for the determination of the spin concentration is about 4% (height of the resonator cavity 23 mm, interval in the resonator center 5 mm). This correction was neglected with regard to the accuracy of the measurement.

The charge passed was measured with a digital coulometer designed and constructed in our department. The voltage drop on its input terminals was less than 1 V. The potentiostat used in the electrolysis was constructed from an operational amplifier of the type AS 101 (Závody prlmyslové automatizace, Trutnov, ČSSR).

The concentration of radical particles was determined with the use of standards with a known quantity of crystalline 1,1-diphenyl-2-picrylhydrazyl (DPPH) (Fluka). The standards were prepared by sucking a benzene solution of DPPH of a known concentration into a piece of glass capillary (length 4—5 mm, measured with a precision to $\pm 0{\cdot}1$ mm) of a known internal diameter (determined by calibration with mercury) and evaporating. This standard was enclosed in a sealed polyethylene capillary (outer diameter about 0·5 mm) and placed in a cuvette together with the sample. For comparison, standards were made also directly by weighing DPPH. The concentration was determined by a two-fold numerical integration of the EPR signal.

Quantum-Chemical Calculations

Quantum-chemical calculations by the Hückel MO method including the calculation of spin populations according to McLachlan were carried our as earlier[7]. The heteroatom model was used to estimate the influence of the methyl group[8].

RESULTS

Electrochemical oxidation of the substances *I*—*VI* was studied by cyclic voltammetry on a platinum electrode in nonaqueous acetonitrile. The potentials corresponding to the maximum current of the first anodic peak and the corresponding voltammetric constants, $i_p/c\sqrt{v}$, are given in Table I. The electrochemical oxidation of compounds *I*—*III* was studied by Ambros and Nelson[1,2]. Our cyclic polarograms of these substances are in good agreement with their results. The behaviour of compounds *IV*—*VI*, studied by us, was not previously published and corresponds to a generalization of the conclusions from ref.[2] for the electro-oxidation of other substituted carbazole derivatives. A comparison of the voltammetric constants $i_p/c\sqrt{v}$ in Table I with a value found for ferrocene under equal conditions (1·38 in the same units) suggests that the first oxidation step in the case of compounds *I*—*V* corresponds to the transfer of more than one electron. With compound *VI*, the voltammetric constant together with the cathodic peak corresponding to the first anodic peak indicates the formation of the most stable primary cation radical of all the studied compounds. Electrolysis of a solution of compound *VI* at the potential of the first anodic peak leads to an intense blue coloration. With compounds *I*—*V*, the electrolysis products are green. In the case of compounds *I*, *III*, and *IV* the electrode is coated with a little soluble, conductive layer of products.

EPR *spectroscopy*. By means of the method of internal electrochemical generation of radicals at a potential by 100 mV more positive than the value of E_p^I, a broad EPR

signal (about 3·5 mT from the maximum to the minimum) was obtained with compound *VI*, which did not show a hyperfine structure.

In the electrolysis of compounds *I*, *III*, and *IV* under the same conditions, a narrow EPR signal (about 0·1 mT from maximum to minimum) was obtained with a g factor equal to 2·0031. It was found by withdrawing the working electrode from the internal generation cell that the EPR signal is bound to a layer of products formed by oxidation on the working electrode. If the latter is withdrawn, the EPR signal is observed even after several days, but if the electrode is left in solution, the EPR signal disappears more rapidly. With compounds *I* and *III*, it decreases to the sensitivity limit of the spectrometer in the course of a day, with compound *IV* it decreases after stopping the electrolysis with a half-time of several minutes. With compounds *II* and *V*, no EPR signal was obtained.

Coulometry in the resonator cavity of EPR *spectrometer.* With compounds *I*, *III*, and *IV*, the dependence of the concentration of particles with an unpaired electron on the charge passed was measured for 30–60 minutes. The measurement was carried out in the resonator cavity of the EPR spectrometer in the cell for internal electrochemical generation of radicals at room temperature. Solutions of the substances in a concentration of 0·001 mol/dm^3 in acetonitrile containing 0·1M-$N(C_2H_5)_4.ClO_4$ were electrolysed at a potential by 0·1 V more positive than the value of E_p^I (Table I). The current was 2–3 μA in a stationary state attained after about 15 min of electrolysis. The dependence of the amount of the formed radicals on the charge

TABLE I

Characteristics of Electrochemical Oxidation of Carbazole Methyl Derivatives

Solutions in nonaqueous acetonitrile with 0·1M-$(C_2H_5)_4NClO_4$; $c(I—VI) = 1 . 10^{-3}$ mol/dm^3. Platinum electrode; sweep rate 0·1 V/s.

	Derivative	E_p^{Ia}	$i_p c^{-1} v^{-1/2}$ [b]
I	carbazole	1·21	3·19
II	9-methyl-	1·14	3·19
III	3-methyl-	1·14	2·98
IV	3,9-dimethyl-	1·09	2·58
V	3,6-dimethyl-	1·10	2·53
VI	3,6,9-trimethyl-	1·06	1·29

[a] Potential (V) corresponding to maximum current of the first anodic peak against S.C.E. (with aqueous NaCl solution). [b] Voltammetric constant for the first anodic peak; i_p (A/cm^2), c (mol/dm^3), v (V/s).

passed are shown in Fig. 1. In all three cases a direct proportionality is observed. With compounds *I* and *III*, the slope of this dependence is reproducible within several percent, with *IV* within about 20 percent.

The current yield of the radicals was determined as 0·019 for compound *I*, 0·016 for *III*, and 0·002 for *IV* (ratio of the number of radical molecules to the number of electrons passed through the electrode).

DISCUSSION

The fact that with compounds *I*–*V*, in whose molecules at least one of the positions 3, 6 or 9 is not blocked with a methyl group, the first step of the electrochemical oxidation corresponds to more than one electron, substantiates the conclusions of Ambros and Nelson[1,2] that these positions are the most reactive centers of the primary cation radical of carbazole. Small differences of the potentials of the first oxidation step, E_p^I, for compounds *I*–*V* against the potential at which a relatively stable primary cation radical of compound *VI* is formed by a one-electron process suggest that the formation of the primary cation radical is the potential-determining step also with substances *I*–*V*. The shift of the values of E_p^I to more negative values in the case of carbazol methyl derivatives is in a qualitative agreement with the HMO approximation of the energy of HOMO, as is apparent from the comparison of the data in Tables I and II.

Fusing of the hyperfine structure of the EPR spectrum of the primary cation radical of compound *VI* can be attributed to its complexity: it consists theoretically of 2268 components. The splitting constants of the EPR spectrum of the cation radical of compound *VI* were estimated on the basis of the splitting constants of the

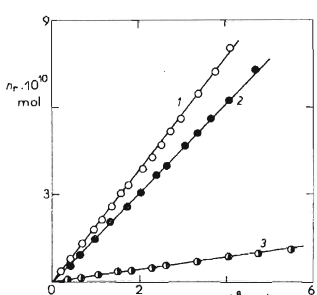


FIG. 1

Dependence of the Mass Quantity of Radical Product, n_r, of Electrochemical Oxidation on Mass Quantity of Electrons Passed, n_e

1 Carbazole; *2* 3-methylcarbazole; *3* 3,9-dimethylcarbazole.

published[10] spectrum of the cation radical of compound *V* and HMO calculations of the spin populations (according to McLachlan) as follows: $a^{H}_{CH_3} = 0{\cdot}68$ mT (1 : 6 : 15 : 20 : 15 : 6 : 1), $a^{H}_{CH_3} = 0{\cdot}75$ mT (1 : 3 : 3 : 1), $a^{H}_1 = 0{\cdot}38$ mT (1 : 2 : 1), $a^{H}_2 = a^{H}_4 = 0{\cdot}08$ mT (1 : 4 : 6 : 4 : 1), $a^{N} = 0{\cdot}8$ mT (1 : 1 : 1). The spectrum simulated with these splitting constants and with $\frac{1}{2}\Delta H_{1/2} = 0{\cdot}07$ mT (half width of non-differentiated line in one half of its height) and larger does not show a hyperfine structure with a Lorentz line form.

The HMO theory predicts for HOMO of carbazole symmetry with respect to the plane of symmetry perpendicular to the plane of the molecule. The form and the energy of HOMO with carbazole and its methyl derivatives are strongly influenced by the choice of the coulombic integral of the N atom and of the resonance integral of the C—N bond. The symmetry of HOMO is, however, preserved if we do not choose a too high value of h_N and a too low value of k_{C-N}. For example, with carbazole the order of MO changes and the place of HOMO is occupied by an orbital of antisymmetrical properties at $h_N \geqq 1{\cdot}8$ and $k_{C-N} \leqq 0{\cdot}8$. In the molecule of compound *V*, this change in the order of the orbitals in the HMO model is attained at $h_N = 1{\cdot}8$ and $k_{C-N} = 0{\cdot}7$ (heteroatomic model of methyl). That the HOMO in carbazole is, in contrast to pyrrole and isoindole[9], symmetrical, is evidenced by the high value of the splitting constant of the N atom ($a^{N} = 0{\cdot}689$ mT (ref.[10])) in the cation radical of compound *V*, further by the dependence of the behaviour of N-substituted

TABLE II
Energy of the Highest Occupied MO of Carbazole Derivatives

	Derivative	m_{HOMO}[a]
I	carbazole	—0·701
II	9-methyl carbazole	—0·640
III	3-methyl carbazole	—0·644
IV	3,9-dimethyl carbazole	—0·595
V	3,6-dimethyl carbazole	—0·615
VI	3,6,9-trimethyl carbazole	—0·565
	1,1′-bicarbazole	—0·511
	3,3′-bicarbazole	—0·526
	3,3′,6′:3″-tercarbazole	—0·495
	3,3′,9′:9″-tercarbazole	—0·453

[a] Energy of the HOMO is defined as $\varepsilon_{HOMO} = \alpha_C - m_{HOMO}\beta_{CC}$; the following parameters were used in calculating HOMO; $h_N = 1{\cdot}5$, $k_{C-N} = 0{\cdot}8$, $k_{N-N} = 0{\cdot}7$; for heteroatomic model of the methyl group $h_{CH_3} = 2$, $k_{C-CH_3} = 0{\cdot}7$, $k_{N-CH_3} = 0{\cdot}6$.

carbazoles in electro-oxidation on the substituent bound on the N atom[1], and by the reactivity of the N atom in cation radicals of carbazoles[1,2].

The value of the spin population p_z-AO of the N atom is with compounds *I*–*VI* in the range 0·15–0·35 depending not only on the compound but mainly on the values of h_N and k_{C-N}. The value of the spin population p_z-AO of the C atom neighbouring with the N atom exceeds in no case 0·05. The spin population p_z-AO of the N atom increases with decreasing h_N and k_{C-N} with all six carbazole derivatives.

With respect to the magnitude of the mentioned splitting constant a^N for the cation radical of compound *V*, we can estimate that the proportionality constant between a^N and spin population p_z-AO of the N atom is 2–4 mT according to the parameters h_N and k_{C-N} used. With respect to the symmetrical properties of HOMO, we can in interpreting the nitrogen splitting in the EPR spectrum neglect the π–σ-spin polarization of the C—N bond caused by the spin population on the neighbouring C atoms in the case of carbazole cation radicals, in contrast to anion radicals of 2,5-dimethyl-1-nitrophenylpyrroles[7] and cation radicals of 1,3,4,7-tetramethylisoindoles[9].

Owing to the small concentration (both relative and absolute) of the insoluble radical product of the oxidation of compounds *I*, *III*, and *IV*, its identification is difficult. The width of the EPR signal shows clearly that we have to deal with a radical in a condensed state. It is apparent that this is not a primary cation radical but probably a cation radical salt of the oxidation product of these compounds with the base electrolyte anion, ClO_4^-. It is probable that this salt is responsible for the conductivity of the layer on the electrode. Ambrose and Nelson[1] showed that dimerization in positions 3 is the dominant reaction of the destruction of the primary cation radical of carbazole in absence of basic substances. According to these authors, carbazole and 3 : 3′-bicarbazole give the same EPR signal during internal electrochemical generation of radicals (although they did not indicate the potential at which the latter compound was electrolysed). However, with compounds *I*, *III*, and *IV* the corresponding 3 : 3′ or 6 : 6′ dimers are oxidizable at the potential of their first oxidation step to the diamagnetic dication. The calculated HOMO energies for certain dimers and trimers of carbazoles in Table II suggest that these compounds are more easily oxidized than carbazole itself. It is, however, possible that when the cation radical salt of the 3 : 3′ or 6 : 6′ dimer is little soluble, the transition into the solid phase causes such an increase of the contribution of the solvation energy to the redox potential that oxidation to a dication becomes energetically impossible. This explanation is supported by the fact that all compounds that on oxidation give a little soluble product of a radical character have at least one of the positions 3 and 6 free (not blocked with methyl). That no EPR signal was obtained during oxidation of 9-methylcarbazole can be attributed to the fact that the cation radical of the 3 : 3′ dimer is much more soluble. With respect to the small quantity of the radical product, the formation of a cation radical of the 1 : 1′ dimer could be also considered (Ambrose and Nelson[1,2] pointed out the reactivity of position 1 in carba-

zole derivatives). Also here, however, it would be necessary to elucidate the behaviour of 9-methylcarbazole by the solubility of products and further to explain why analogous radical products are not formed during oxidation of compounds *V* and *VI*. The elucidation of the observed EPR signal in terms of radicals of trimeric carbazoles is very doubtful because of the occurrence of this signal during electrochemical oxidation of 3-methylcarbazole and especially 3,9-dimethylcarbazole.

The absence of the EPR signal in the case of compound *II* is according to Ambrose and Nelson[1] caused by the fact that an extremely stable dimer is formed by oxidation, hence further oxidation is possible at a much more possitive potential. According to these authors[2], oxidation of 3,6-disubstituted carbazoles (such as compound *V*) is followed by rapid dimerization either in positions 1,1′ or 1,9′ or 9,9′, so that the half-time of the radicals is 0·1 – 1 s. Indeed, no EPR signal was obtained with compound *V*.

The formation of a little soluble cation radical salt of the 3 : 3′ or 6 : 6′ dimer is therefore most probably responsible for the EPR signal observed during internal electrochemical generation of radicals in the oxidation of carbazole, 3-methylcarbazole, and 3,9-dimethylcarbazole. Different current yields of the radicals can be in the case of compounds *I*, *III*, and *IV* attributed to different solubility of cation radical salts and other products adhering to the electrode.

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