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Original scientific paper

Molecular-orbital and structural descriptors in theoretical investigation of electroreduction of nitrodiazoles

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Abstract: It is shown how a simple theoretical approach can be used for the investigation of electro-organic reactions. Mononitroimidazoles and mononitropyrazoles were studied by the semiempirical MNDO-PM3 molecular orbital method. The electrochemical reduction potentials of diazoles have been correlated with the energy of the lowest unoccupied molecular orbital (LUMO). It was found that an admirable correlation could be obtained by the introduction of simple structural descriptors as a correction to the energy of the LUMO. The interaction of a molecule with its surrounding depends on electrostatic potential and on steric hindrance. Most of these steric effects are taken into account using two parameters having a very limited set of integer values. The first (β) is the position of a ring substituent regarding ring nitrogens, which accounts for the different orientations of dipole moments and for the different shape of the electrostatic potential. The second (structural) parameter (τ) is the type of the ring, which accounts mostly for different modes of electrode approach, and for different charge polarization patterns in two diazole rings. The extended correlation with E_{LUMO}, β and τ, is very good, having a regression coefficient $r = 0.991$. The intrinsic importance of β and τ is exemplified by their high statistical weight.

Keywords: reduction potentials, PM3-MNDO, LFER, nitrodiazoles, structural descriptors.

INTRODUCTION

Nitro compounds have attracted the attention of electrochemists from the first days of polarographic investigations. The first synthesized nitro compound was nitrobenzene, which was synthesized by the Mitscherlich reaction[1] in 1884, and it was also the first organic compound studied by the polarographic technique.[1–3] After the year 1925, many organic, especially nitro compounds, have been studied electrochemically[2–6] and for many of them the mechanisms of their reduction were explained. Since many nitrodiazoles are pharmaceutically active compounds, the

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understanding of the reduction process of these compounds is crucial for basic medicinal chemistry, as well as for the pharmaceutical industry. From the very beginning, these compounds have found many applications. They have been used as chemotherapeutics (antibacterial, antitrichomonal and antihistomonal (antiriprotozoal) agents[6]) and as radiosensitizers in medical practice. The capability of nitrodiazoles to bind to DNA and block their replication[4,7,8] could have many applications in antiviral therapy.

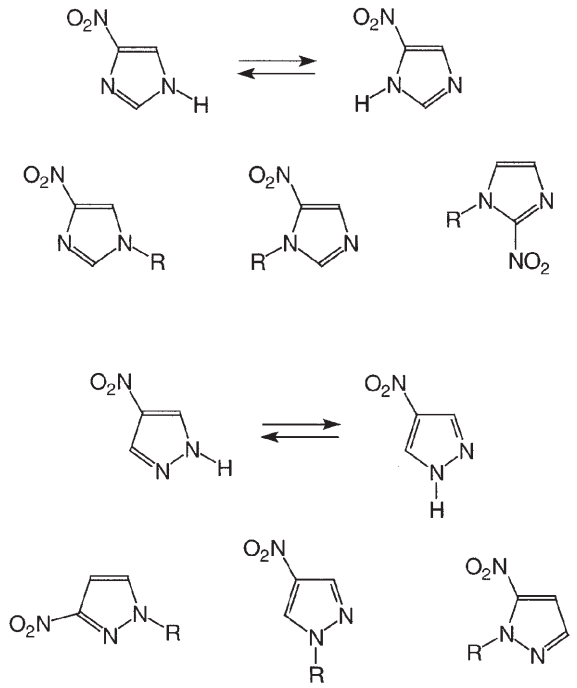
The differences in the electrochemical behaviour of nitropyrazoles and nitro imidazoles are explained by different sequences of electron/proton transfer steps during the reduction process. The reasons for these differences are beyond electrochemistry and can be explained by the different electronic structure of pyrazoles and imidazoles. The macroscopic electrochemical reduction potential is a complex balance of inductive, steric and solvation effects. Inductive effects are well described by the LUMO energy. Correlation of the measured potentials with the LUMO energy is fairly good, but not good enough for quantitative predictions.

THEORETICAL BACKGROUND

A simple electroorganic reaction is a heterogeneous process involving three different steps: adsorption, electron-transfer, and desorption. The most important step in the process is the electron transfer. The electron transfer occurs between an organic molecule adsorbed at the electrode and the electrode itself (the cathode in the case of a reduction process). The molecular orbital picture of electron transfer describes it as a process in which the organic molecule attains a transitory state at the electrode due to an electron transfer from the electrode to the lowest unoccupied molecular orbital (LUMO) of the molecule.[5] The rate of electron transfer depends on the coupling of the electronic states of all molecules involved, and on nuclear fluctuations necessary to bring these states into resonance.[9,10] Theories which deal more quantitatively with electron transfer, adiabatic or non-adiabatic, are described elsewhere.[9–11] It is important to stress that in organic electrochemical reactions and in biochemical processes, a strong coupling between electron and proton transfer[2,6,10,11] occurs, and these couplings make the reduction mechanism much more complex.

The electroactivity of mononitrodiazoles is ehnanced by the presence of a nitro group on the diazole ring. The structures of nitrodiazoles are presented in Scheme 1. The reduction of mononitro diazoles is a four-electron process, in which the nitro group is transformed to a hydroxylamine group (Eq. (1)). When the nitro group is the electroactive group on the diazole ring, the replacement of one ring aliphatic substituent with another aliphatic group does not change the value of the half-wave potential.[2–6]

$$ArNO_2 + 4\ e^- + 4\ H^+ \rightarrow ArNHOH + H_2O \qquad (1)$$



Scheme 1. Chemical structures of nitroimidazoles and nitropyrazoles derivatives. (R Indicates a methyl or an ethyl group.)

The general stoichiometry of the electrochemical reduction of all diazoles is the same, and is given by Eq. (1), but the sequences of the elementary steps in the electro-chemical reduction[1] of pyrazoles and imidazoles are considered to be different. In the case of alkylnitro pyrazoles, prior to the rate-determining step of the reduction, two electrons and three protons have to be transferred. The sequence in the reduction steps of alkylnitro pyrazoles is H^+, e^-, H^+, H^+, e^-, $2e^-$, H^+; but in the case of alkylnitro imidazoles, the sequence is H^+, H^+, e^-, H^+, e^-, $2e^-$, H^+. It is important to stress that *N*-unsubstituted nitroazoles have an additional acid-base equilibrium, which affects the different steps in the reduction process regarding the substituted derivatives.[2]

METHOD

Mononitrodiazoles were investigated by semiempirical molecular-orbital methods using the program package MOPAC 7.01.[12,13] The PM3 method[12–15] was used for optimising all the structures in the neutral form and all possible protonated forms of the bases. The PM3 method was developed by Stewart in 1989 as an improvement to the MNDO-AM1 method, changing the optimisation technique for parameterisation and fitting to a much more extensive database of physical properties, with the emphasis on nitro compounds. For the calculation of the energy of the LUMO, a CI calculation was included, involving the active space of two frontier orbitals.

The MO parameters for MNDO-PM3 were optimized so as to reproduce the

experimental heat of formation (*i.e.*, the standard enthalpy of formation, $\Delta_f H$, or the enthalpy change to form a mole of compound at 25 ºC (298 K) from its elements in their standard state), as well as observed geometries (mostly at 25 ºC).[9]

All molecular structures were optimized according to the PM3 force field in vacuum. For the geometry optimization in a polar medium, the solvent was modelled as a dielectric continuum (COSMO model)[12,13,16,17] with a dielectric constant for water of 78.4. (The solvent is treated as a perturbation of the gas phase system.) A significant difference between the optimized structures in the gas phase and in the solution has been found.

The MO parameters for MNDO-PM3 are optimized so as to reproduce the experimental heat of formation (*i.e.*, the standard enthalpy of formation or the entalpy of change to form a mole of compound at 25 ºC (298 K) from its elements in their standard state), as well as observed geometries (mostly at 25 ºC).[13]

RESULTS AND DISCUSSION

Tables I, II and III show that diazoles with a nitro group in position 4 of the ring are the most stable. The data also show that all the imidazole derivatives are more stable[2,4,6,18] than the corresponding pyrazoles. The calculated data were compared with the experimental data obtained at pH 6.1, because at this pH all molecules are in their neutral form (non-ionic). The agreement with the experimental results was excellent,[2,7] confirming that the semiempirical PM3 method is reliable for the optimisation of organic molecules.

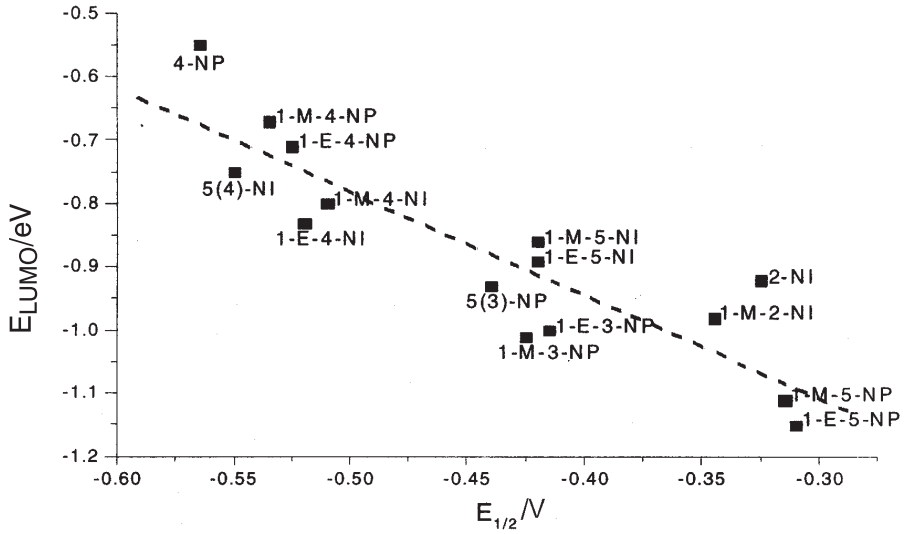


Fig. 1. Correlation of $E_{1/2}$ versus E_{LUMO} calculated with the simulation of an aqueous solution (r = 0.885).

The measured half-wave potentials are summarised in Table IV. It should be noted that unsubstituted diazoles could undergo hydrogen exchange between the

TABLE I. Thermodynamic data calculated using the MNDO-PM3 method for various prototropes of unsubstituted nitroimidazoles and nitropyrazoles

Compound	Molecular species	$\Delta_f H°$/kJ mol^{-1}		E_{HOMO}/eV		E_{LUMO}/eV	
		Gas	H_2O	Gas	H_2O	Gas	H_2O
2-Nitroimidazole	Neutral	85.94	– 55.77	– 10.51	– 10.08	– 1.05	– 0.92
	Protonated pyrrole nitrogen	765.09	456.14	– 4.75	– 9.51	– 4.94	– 0.65
	Protonated nitro group	857.6	517.56	– 15.21	– 10.72	– 6.92	– 2.34
4-Nitroimidazole	Neutral	78.99	– 75.48	– 10.62	– 10.19	– 0.70	– 0.74
	Protonated pyrrole nitrogen	761.61	374.51	– 16.21	– 10.61	– 6.13	– 0.55
	Protonated nitro group	819.14	495.18	– 15.45	– 12.09	– 6.58	– 3.78
5-Nitroimidazole	Neutral	70.25	– 73.35	– 10.70	– 10.31	– 1.08	– 0.77
	Protonated pyrrole nitrogen	761.61	374.68	– 16.21	– 12.80	– 6.13	– 3.15
	Protonated nitro group	855.72	497.85	– 15.42	– 11.02	– 6.87	– 2.22
3-Nitropyrazole	Neutral	37.93	5.24	– 10.90	– 10.41	– 0.82	– 0.91
	Protonated pyrrole nitrogen	221.79	125.30	– 16.14	– 10.64	– 6.80	– 1.29
	Protonated nitro group	219.45	143.04	– 15.44	– 11.92	– 6.78	– 3.89
4-Nitropyrazole	Neutral	143.72	3.35	– 10.93	– 10.46	– 0.82	– 0.49
	Protonated pyrrole nitrogen	924.29	502.83	– 15.87	– 10.70	– 6.54	– 0.43
	Protonated nitro group	898.89	564.76	– 15.74	– 11.68	– 6.74	– 3.24
5-Nitropyrazole	Neutral	153.38	28.99	– 10.72	– 10.22	– 1.21	– 0.93
	Protonated nitrogen	927.97	535.47	– 16.14	– 10.96	– 6.80	– 1.59
	Protonated nitro group	947.25	611.37	– 15.20	– 10.50	– 7.05	– 2.10

TABLE II. Thermodynamic data calculated using the MNDO-PM3 method for various prototropes of methyl nitroimidazoles and methyl nitropyrazoles

Compound	Molecular species	$\Delta_f H^o$/kJ mol^{-1}		E_{HOMO}/eV		E_{LUMO}/eV	
		Gas	H_2O	Gas	H_2O	Gas	H_2O
1-Methyl-2-nitroimidazole	Neutral	85.48	– 38.03	– 10.37	– 10.16	– 0.97	– 1.06
	Protonated pyrrole nitrogen	751.11	434.72	– 15.83	– 11.14	– 6.27	– 1.43
	Cation on nitro group	837.76	539.74	– 15.13	– 10.62	– 6.71	– 2.17
1-Methyl-4-nitroimidazole	Neutral	71.55	– 66.73	– 10.50	– 10.27	– 0.65	– 0.79
	Protonated pyrrole nitrogen	742.49	412.63	– 15.95	– 10.62	– 5.94	– 0.39
	Protonated nitro group	801.70	506.26	– 15.21	– 11.68	– 6.44	– 3.32
1-Methyl-5-nitroimidazole	Neutral	69.37	– 49.71	– 10.52	– 10.30	– 1.02	– 0.86
	Protonated pyrrole nitrogen	747.14	438.19	– 15.93	– 10.58	– 5.94	– 0.60
	Protonated nitro group	845.84	518.15	– 15.28	– 10.90	– 6.72	– 2.11
1-Methyl-4-Nitropyrazole	Neutral	136.82	13.39	– 10.63	– 10.35	– 0.77	– 0.57
	Protonated pyrrole nitrogen	895.79	512.54	– 15.72	– 11.51	– 6.34	– 1.43
	Protonated nitro group	880.52	573.75	– 15.27	– 10.87	– 6.51	– 1.80
1-Methyl-3-Nitropyrazole	Neutral	155.14	30.21	– 10.63	– 10.41	– 0.77	– 1.01
	Protonated pyrrole nitrogen	900.19	595.30	– 15.84	– 10.57	– 6.60	– 1.20
	Protonated nitro group	900.86	612.41	– 15.30	– 11.01	– 6.63	– 2.30
1-Methyl-5-Nitro-pyrazole	Neutral	153.26	46.53	– 10.40	– 10.13	– 1.15	– 1.11
	Protonated pyrrole nitrogen	905.84	549.78	– 15.71	– 10.92	– 6.60	– 1.76
	Protonated nitro group	936.88	623.50	– 14.90	– 10.82	– 6.89	– 2.61

TABLE III. Thermodynamic data calculated using the MNDO-PM3 method for various prototropes of ethyl nitroimidazoles and ethyl nitropyrazoles

Compound	Molecular species	$\Delta_f H^o$ / kJ mol^{-1}		E_{HOMO} / eV		E_{LUMO} / eV	
		Gas	H_2O	Gas	H_2O	Gas	H_2O
1-Ethyl-2-nitroimidazole	Neutral	62.26	– 51.00	– 10.33	– 10.22	– 0.89	– 1.09
	Protonated pyrrole nitrogen	723.96	398.90	– 15.74	– 11.00	– 8.19	– 1.44
	Protonated nitro group	809.86	526.05	– 15.06	– 10.70	– 6.65	– 2.28
1-Ethyl-4-nitroimidazole	Neutral	49.83	– 89.20	– 10.45	– 10.32	– 0.60	– 0.83
	Protonated pyrrole nitrogen	711.36	364.68	– 15.96	– 11.10	– 5.86	– 0.82
	Protonated nitro group	781.78	486.89	– 14.93	– 11.01	– 6.42	– 2.24
1-Ethyl-5-nitroimidazole	Neutral	48.24	– 72.22	– 10.50	– 10.37	– 0.97	– 0.89
	Protonated pyrrole nitrogen	720.65	377.19	– 15.86	– 12.36	– 5.85	– 2.40
	Protonated nitro group	816.38	509.11	– 15.26	– 11.03	– 6.64	– 2.23
1-Ethyl-4-nitropyrazole	Neutral	111.09	– 11.17	– 10.64	– 10.52	– 0.73	– 0.71
	Protonated pyrrole nitrogen	862.66	494.97	– 15.66	– 11.03	–6.23	– 1.12
	Protonated nitro group	851.78	554.42	– 15.30	– 11.20	– 6.47	– 2.05
1-Ethyl-3-nitropyrazole	Neutral	121.71	9.54	– 10.62	– 10.49	– 0.75	– 1.00
	Protonated pyrrole nitrogen	867.34	530.82	– 15.77	– 10.92	– 6.50	– 1.57
	Protonated nitro group	873.70	593.58	– 15.18	– 12.23	– 6.56	– 4.38
1-Ethyl-5-nitropyrazole	Neutral	131.00	29.58	– 10.42	– 10.24	– 1.12	– 1.15
	Protonated pyrrole nitrogen	877.30	538.48	– 15.55	– 10.91	– 6.46	– 1.58
	Protonated nitro group	910.56	620.53	– 14.87	– 10.78	– 6.82	– 2.50

TABLE IV. Experimental values*+ of the half-wave reduction potentials at pH = 6.1

Compound	$E_{1/2}$/V
4(5)-Nitroimidazole	– 0.55
2-Nitroimidazole	– 0.325
1-Methyl-2-nitroimidazole	– 0.345
1-Methyl-5-nitroimidazole	– 0.42
1-Ethyl-5-nitroimidazole	– 0.42
1-Methyl-4-nitroimidazole	– 0.51
1-Ethyl-4-nitroimidazole	– 0.52
4-Nitropyrazole	– 0.565
5(3)-Nitropyrazole	– 0.44
1-Methyl-5-nitropyrazole	– 0.315
1-Ethyl-5-nitropyrazole	– 0.31
1-Methyl-3-nitropyrazole	– 0.425
1-Ethyl-3-nitropyrazole	– 0.415
1-Methyl-4-nitropyrazole	– 0.535
1-Ethyl-4-nitropyrazole	– 0.525

*Values were reported in references 2, 7 and 27

+The half-wave potential was measured using a mercury dropping electrode (DME) as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. The measured potential was corrected to the value of the reduction potential of a Tl^{2+} salt in the same buffer. This procedure is a standard procedure in organic electrochemistry (see Zuman and Dumanović).[2,6,18]

nitrogen atoms in the ring (Scheme 1). Therefore, the 5- and 4-nitroimidazoles could not be distinguished on the electrode. The same applies with 5- and 3-nitropyrazoles. For the correlations, the more stable calculated structures were used, *i.e.*, 5-nitropyrazole and 4-nitroimidazole. The energy of the lowest unoccupied MO is considered to be the major feature of the electronic structure which is important for the reduction process. For all nitrodiazoles, the LUMO is heavily localised on the nitro group. The correlation between the LUMO and the half-wave potential of different nitrodiazoles (Figure 1) shows the well known linear dependence, as in many similar correlations published elsewhere.[14,15,19–21] The straight correlation of the experimental $E_{1/2}$ to the calculated E_{LUMO} is rather poor (Fig. 1; $r = 0.885$, constant = –1.597, coefficient = –1.632). The different molecular structures of the various nitrodiazoles (imidazoles and pyrazoles) may influence processes such as adsorption, solvation and orientation at the electrode. These processes precede the electron transfer step and affect the half-wave potential. In order to improve the correlation and account for structural differences between the various nitrodiazoles, the reduction potential was corrected by two topological parameters (Eq. (2)). These parameters address the steric and electronic differences of the various nitrodiazoles.

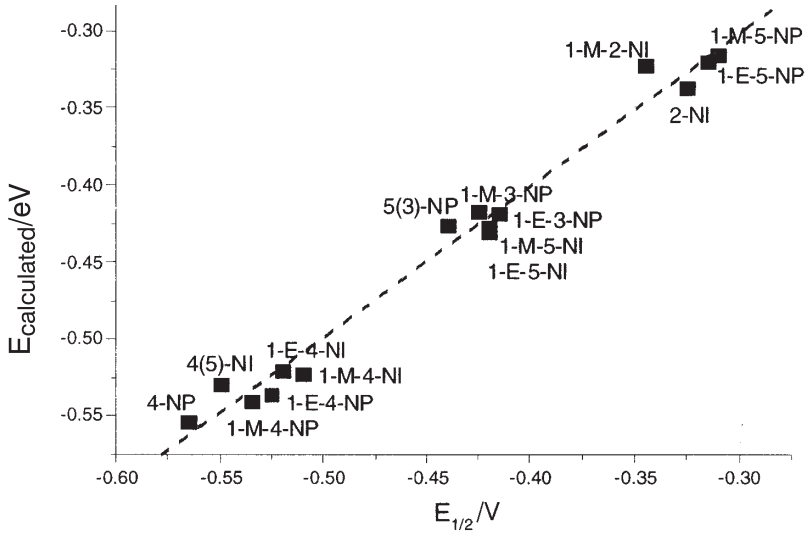


Fig. 2. Reduction potentials calculated according to Eq. (3), correlated with the experimental electrode half-wave reduction potential (r = 0.991).

$$E_{1/2} = A \cdot E_{\mathrm{LUMO}} + B \cdot \beta + C \cdot \tau + D \qquad (2)$$

β and τ are topological parameters which have discrete values. Similar steric and topological descriptors of molecules are frequently used in QSAR investigations[7] of biologically active compounds in medicinal chemistry, as well as in physical organic chemistry.[22]

TABLE V. Correlation of the electrode reduction potential of nitrodiazoles with MO and topological parameters

	$E_{1/2}$/V	E_{LUMO}/eV	β (vicinity)	τ (ring type)	$E_{\mathrm{calc}}{}^{*}$/V
4(5)-Nitroimidazole	– 0.55	– 0.74	1	0	– 0.530
2-Nitroimidazole	– 0.325	– 0.92	3	0	– 0.337
1-Methyl-2-nitroimidazole	– 0.345	– 1.06	3	0	– 0.322
1-Methyl-5-nitroimidazole	– 0.42	– 0.86	2	0	– 0.430
1-Ethyl-5-nitroimidazole	– 0.42	– 0.89	2	0	– 0.427
1-Methyl-4-nitroimidazole	– 0.51	– 0.8	1	0	– 0.524
1-Ethyl-4-nitroimidazole	– 0.82	– 0.83	1	0	– 0.520
4-Nitropyrazole	– 0.565	– 0.55	0	1	– 0.554
5(3)-Nitropyrazole	– 0.44	– 0.93	1	1	– 0.426
1-Methyl-5-nitropyrazole	– 0.315	– 1.11	2	1	– 0.320
1-Ethyl-5-nitropyrazole	– 0.31	– 1.15	2	1	– 0.316
1-Methyl-3-nitropyrazole	– 0.425	– 1.01	1	1	– 0.418

TABLE V. Continued

	$E_{1/2}$/V	E_{LUMO}/eV	β (vicinity)	τ (ring type)	E_{calc}*/V
1-Ethyl-3-nitropyrazole	– 0.415	– 1	1	1	– 0.419
1-Methyl-4-nitropyrazole	– 0.535	– 0.67	0	1	– 0.541
1-Ethyl-4-nitropyrazole	– 0.525	– 0.71	0	1	– 0.537

* Equation (3).

The parameter β reflects the environment of the nitro group regarding its position in the ring, and has different values for the three possible situations: $\beta = 2$ when the nitro group is in the neighbourhood of the pyrrolic nitrogen; $\beta = 1$ when the nitro group is in the neighbourhood of the pyridinic nitrogen and $\beta = 0$ when the nitro group is not in the neighbourhood of the ring nitrogen.

Consequently, for 2-nitroimidazole, where the nitro group is in the neighbourhood of both ring nitrogens: $\beta = 2 + 1 = 3$. Since only the nitro group is electrochemically active, this descriptor must diminish the difference due to the different positions of the nitro group on the diazole ring.

Parameter τ simply denotes the ring type. It is equal to zero for one ring type and non-zero for the other one. The following values were used:

$\tau = 1$ for the pyrazole ring, and $\tau = 0$ for the imidazole ring.

A reversed choice would do equally well. This τ parameter is related to the already mentioned difference in the sequence of the electrode reactions of pyrazoles and imidazoles.

Using these descriptors, a corrected half-wave potential (the last column in Table V) was calculated according to the following equation obtained by multilinear regression analysis ($r = 0.991$, Fig. 2).

$$E_{calc} = - 0.107 \, (E_{LUMO} - 0.812 \, \beta - 0.779 \, \tau) - 0.696 \qquad (3)$$

When the topological parameters are taken into account, the correlation is significantly improved (Fig. 2), as confirmed by the high value of the regression coefficient ($r = 0.991$).

It must be emphasized that the β parameter includes different effects, which could influence the mode of the approach of a molecule to the electrode, such as molecular electrostatic potential, the key parameter determining the orientation of molecules to the electrostatic potential, and the adsorption process. The steric parameters from the Hammett equations[23,24] are also implicitly included in this parameter.

Equation (3) also shows that the weights of all the selected parameters are remarkably similar. This means that the selected topological parameters have a definite physical significance. The intrinsic importance of β and τ is exemplified by their high statistical weights. The necessity of using coupled β and τ parameters could be rationalized on the basis of alternating charge polarizations[25] in diazoles ring. The two nitrogens in the imidazole ring induce the same kind of charge polarizations on the ring carbon atoms and on the ring substituents, in contrast to the

pyrazole ring, where the two nitrogens induce opposite charge polarizations on other atoms in the molecule. It is important to stress that for a precise molecular description of the electrochemical behaviour of nitrodiazoles, especially of their halogenated derivatives, more theoretical work would be needed.

CONCLUSION

The electrochemical reduction of nitrodiazoles is a four-electron process with different sequences of the electron and proton steps for imidazoles and pyrazoles. These differences are caused by the different electronic structures of pyrazoles and imidazoles. In order to improve the correlation between the energy of the LUMO orbital and the half-wave potential, the potential was corrected by two topological parameters having a small set of integer values. The first (β) compensates for the differences caused by the different position of the nitro group on the diazole ring, and the second topological parameter (τ) compensates the differences in the type of the ring. The correlation was significantly improved with these corrections indicating that these parameters have a physical background related to the structure of the molecule.

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ИЗВОД

МОЛЕКУЛСКО-ОРБИТАЛНИ И СТРУКТУРНИ ДЕСКРИПТОРИ КОД ТЕОРИЈСКОГ ПРОУЧАВАЊА ЕЛЕКТРОРЕДУКЦИЈЕ НИТРОДИАЗОЛА

БРАНКО КОЛАРИЋ, ИВАН ЈУРАНИЋ и ДРАГИЦА ДУМАНОВИЋ

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У овом чланку је показано како се прост теоријски приступ може применити код проучавања електроорганских реакција. Проучавали смо мононитроимидазоле и мононитропиразоле помоћу семиемпиријске MNDO-PM3 молекулско-орбиталне методе. Електрохемијски редукциони потенцијал диазола је корелисан са енергијом најниже непопуњене молекулске орбитале (LUMO). Нађено је да се добија изврсна корелација увођењем простих структурних дескриптора као корекције за LUMO енергију. Интеракција молекула са околином зависи од електростатичког потенцијала и стерних сметњи. Већина ових стерних ефеката је узета у обзир коришћењем два параметра који имају врло ограничен скуп целобројних вредности. Један (β) је положај супституента на прстену у односу на азотове атоме прстена, чиме се води рачуна о различитим оријентацијама диполних момената и о различитом облику електростатичког потенцијала. Други (структурни) параметар (τ) јесте тип прстена, чиме се урачунава углавном различит начин приласка два диазолска прстена електроди, као и различита поларизација наелектрисања у њима. Проширена корелација са E_{LUMO}, β, и τ, веома је добра, са регресионим коефицијентом $r = 0.991$. Суштински значај β и τ је исказан кроз њихову велику статистичку тежину.

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