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Electrochemical, ESR and quantum chemical study of 1-substituted naphthalenes and their radical anions^{†,‡}

N. V. Vasilieva^a*, I. G. Irtegova^a, T. A. Vaganova^a and V. D. Shteingarts^{a,b}*

Electrochemical reduction and oxidation of a series of 1-substituted naphthalenes (1-X-naphthalenes) have been studied by the method of cyclic voltammetry (CV). The first reduction peak of the majority of these compounds corresponds to a one-electron transfer to form the relatively stable radical anion (RA). For these species, ESR spectra have been registered and interpreted, the life time has been estimated. The first oxidation peaks of 1-X-naphthalenes are irreversible and correspond to a transfer of two or more electrons. Copyright © 2007 John Wiley & Sons, Ltd.

Keywords: electrochemical reduction; electrochemical oxidation; radical anions; radical cations; ESR spectroscopy; cyclic voltammetry; naphthalene derivatives

INTRODUCTION

One-electronic reduction and oxidation of aromatic compounds with the formation of rather stable radical ions (RIs) is the perspective approach to arene activation for various transformations as occurrence of powerful reactivity factors such as a charge and an unpaired electron is combined with conservation of structural integrity.^[2] For purposeful use of this approach, electrochemical characteristics of activated compounds and data on the electronic structure of their RIs are important. From this point of view, the study of one-electron reduction and oxidation of substituted arenes by the cyclic voltammetry (CV) method is relevant to obtain electrochemical potential values reflecting their frontier MO energies and, besides, to estimate a stability of RIs thus formed. Additionally, their ESR spectra give an information on the spin density distribution. All these characteristics are useful for the interpretation of their reactivity and create the basis for a tentative prediction of arene reaction ways with the RI intermediacy.

Benzene derivatives were electrochemically studied quite intensively.^[3] At the same time, the higher electron affinity and the smaller ionization potential of naphthalene in comparison with benzene are favourable to a wider substituent variation in the RIs which are stable enough to be generated in preparative concentrations and suitable as synthons. There are the numerous publications on the electrochemical reduction of 1-X-naphthalene derivatives,^[4] but these data are incommensurable because of the great variety of experimental conditions. The oxidation potential values are available mainly for naphthalene derivatives with electron-donating substituents,^[5] and from those with electron-withdrawing substituents - only for naphthalenes with the CN, NO₂ and COOH groups.^[6] The ESR data are known only for radical anions (RAs) of 1-X-naphthalenes with X = H, CH_3 , CNand NO2.^[7-9] Thus, stability of formed RAs in most of the cases was not characterized.

In this connection, the goal of the present work is the CV study of electrochemical reduction and oxidation of 1-X-naphthalenes $(X = H (1), CH_3 (2), OCH_3 (3), CO_2CH_3 (4), CONH_2 (5), CON(CH_3)_2 (6), CN (7), COPh (8), COCH_3 (9), CHO (10), NO_2 (11)) in CH_3CN, the estimation of the substituent X influence on the electrochemical potential values and stability of the resulting Rls and elucidation of their electronic structure by means of ESR spectroscopy.$

EXPERIMENTAL

CV measurements on 2×10^{-3} mol/L solutions of **1–11** were performed using CVA-1BM potentiostat equipped with a LAB-MASTER analogue-to-digital converter with multifunctional interface (Institute of Nuclear Physics, Russian Academy of Sciences, Novosibirsk), which enables complete digital control of the system. The measurements were carried out in a mode of triangular pulse potential sweep in three-electrode electrochemical cell, at 295 K in an argon atmosphere in absolute DMF or CH₃CN solution of 0.1 M (n-C₄H₉)₄NBF₄ as supporting electrolyte at a stationary platinum electrode (S = 8 mm²), with sweep rates of 0.01–100 V/s. Peak potentials are quoted with reference to a saturated calomel electrode. DMF was twice vacuum distilled over P₂O₅. CH₃CN was distilled over KMnO₄ and twice over P₂O₅.

ESR spectra were recorded on Bruker ESP-300 spectrometer (MW power 265 mW, modulation frequency 100 KHz, modulation

* N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mails: vasileva@nioch.nsc.ru; shtein@nioch.nsc.ru

 N. V. Vasilieva, I. G. Irtegova, T. A. Vaganova, V. D. Shteingarts
N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation

b V. D. Shteingarts

Novosibirsk State University, 630090 Novosibirsk, Russian Federation [†]Dedicated to the memory of Academician N. N. Vorozhtsov on the occasion of his 100th birthday.

[‡]Reductive activation of arenes. Part 23; for Part 22 see Ref. [1].



electron affinities (EA ₁) and adiabatic ionization energies (IE_1)							
Compound (X)	$E_{\rm p}^{\rm 1C}$ (V)	EA ₁ (eV)	$\nu^{rev} (\geq V/s)^a$	$E_{\rm p}^{\rm 2C}$ (V)	$E_{\rm p}^{\rm 1Ox}$ (V)	IE ₁ (eV)	
1 (none)	-2.61	0.312	≥0.05	_	1.72	-5.274	
2 (CH ₃)	-2.66	0.289	≥0.10	_	1.61	-5.147	
3 (OCH ₃)	-2.74	0.390	≥0.10	_	1.33	-4.844	
4 (CO ₂ CH ₃)	-1.99	-0.523	0.02 ^b	_	1.94	-5.462	
5 (CONH ₂)	-2.16	-0.411	≥0.10	_	1.89	-5.415	
6 (CON(CH ₃) ₂)	-2.38	-0.239	\geq 2	_	1.80	-5.187	
7 (CN)	-1.96	-0.625	0.02 ^b	_	2.11	-5.809	
8 (COPh)	-1.78	-0.737	0.01 ^b	-2.27	1.88	-5.434	
9 (COCH ₃)	-1.86	-0.744	0.02 ^b	-2.44	1.88	-5.464	
10 (CHO)	-1.69	-0.763	≥0.20	—	1.98	-5.691	
In DMF	-1.66		0.01 ^b	-2.31			
11 (NO ₂)	-1.12	-1.292	0.01 ^b	-1.92	2.13	-5.950	
^a The sween rate at w	which a anode nea	ak 1A in the reverse	part of reduction CV	becomes observa	ble		

Table 1 Experimental redox potentials of 1-X-paphthalenes 1-11 in CH₂CN (y = 100 my/s) their gas phase DET RIYP/37 first

^b Anode peak 1A at this scan rate is sufficiently intensive, at a smaller scan rate the experiment is not carried out.

amplitude 0.005 mT) equipped with rectangular double resonator and BST-100/700 temperature control unit. For ESR measurements, DMF solutions $(1-5 \times 10^{-3} \text{ M})$ of 1-X-naphthalenes were reduced on a Pt electrode in anaerobic conditions at the first peak reduction potential and T = 295 K (for 2, 4, 7–11, Table 1), T = 243 K (for 3) with 0.1 M Bu₄NBF₄ as supporting electrolyte. Digital simulation of ESR spectra was carried out using the Winsim 2002 program. Accuracy in calculating a values is \pm 0.0001 mT. The RA half-life values ($\tau_{1/2}$) were calculated by adjusting the time dependences of the ESR integral intensities (starting from the moment of potential switching-off) to an equation for the first-order RA decay ($l = Ae^{-k\bar{t}} + B$, $\tau_{1/2} =$ 0.69 k⁻¹). DFT BLYP/3z calculations of full and frontier MO energies of neutral compounds and RAs were performed using the program 'Nature 2.02'^[10] with full optimization of molecular geometry. The orbital basis sets of size {3,1,1/1} for H and {6,1,1,1,1,1/1,1} for C, N, O were used for DFT calculations.

1-X-Naphthalenes were prepared and purified as described below.

1-Methoxynaphthalene was purified by high vacuum (0.01 mm Hg) distillation.

1-Methylnaphthalene was purified by distillation, b.p. 58–60°C/ 1 mm Hg, lit.^[11] b.p. 111°C/12 mm Hg.

1-Naphthonitrile was purified by sublimation, m.p. 37-38°C, lit.^[11] m.p. 38°C.

1-Nitronaphthalene was purified by crystallization from EtOH, m.p. 60–61°C, lit.^[11] m.p. 57.8°C.

1-Naphthaldehyde was purified through the formation of bisulphate derivatives and distillation, b.p. 111-113°C/1 mm Hg, lit.^[11] b.p. 144°C/4 mm Hg, purity 97.8%, 2-naphthaldehyde admixture 1.9%.

1-Naphthamide was prepared according to the procedure,^[12] m.p. 205°C (from EtOH), lit.^[11] m.p. 205°C.

N,N-Dimethyl-1-naphthamide was prepared by the interaction of naphthoyl chloride with DMF according to the procedure,^[13] m.p. 62–62.5°C (from hexane), lit.^[14] m.p. 62–63°C.

1-Carbomethoxynaphthalene was prepared by the esterification of 1-naphthoic acid with MeOH in the presence of H₂SO₄, m.p. 58–59°C (from hexane), lit.^[15] m.p. 58–60°C.

1-Acetylnaphthalene was prepared by the interaction of naphthyl magnesium bromide with CH₃CN according to the procedure^[16] and purified by chromatography, m.p. 9–10°C (from hexane), lit.^[11] m.p. 10.5°C.

1-Benzoylnaphthalene was prepared by the interaction of naphthalene with benzoyl chloride in the presence of AlCl₃ according to the procedure^[11] and purified by two-fold crystallization from EtOH, m.p. 73-73.5°C, lit.^[14] m.p. 73°C.

RESULTS AND DISCUSSION

The values of reduction and oxidation potentials of 1-Xnaphthalenes 1–11 (X = H, CH_3 , OCH_3 , CO_2CH_3 , $CONH_2$, CON(CH₃)₂, CN, COPh, COCH₃, CHO, NO₂) obtained in the present work by using the CV method in CH₃CN on a stationary Pt electrode are listed in Table 1. As an example, the cyclic voltamograms of reduction (Fig. 1a) and oxidation (Fig. 1b) of 7 are presented in Fig. 1. Depending on the X substituent, one or two reduction peaks are observed on a cathodic curve of the voltammogram. For the most of compounds investigated the first reduction peak 1C is diffusionally controlled $(i_p v^{-1/2} = \text{const},$ where i_p is the peak current and ν is a potential sweep rate), reversible or quasireversible ($E_{p}^{1A} - E_{p}^{1C} = 0.06 \text{ V}, E_{p/2}^{1C} - E_{p}^{1C} = 0.06 \text{ V}$) and corresponds to the one-electron transfer.

Depending upon substituents, the first reduction peak potential changes from $-1.12 V (X = NO_2)$ to $-2.74 V (X = OCH_3)$. A good linear correlation (r = 0.988) exists between the E_n^{1C} values and the σ_{para}^{-} constants for electron-accepting substituents, the point for X = CN being only deviating. The same situation we observed for the benzene derivatives.* Respectively, a satisfac-

^{*}The values of peak potentials of C_6H_5X and σ_{para}^- – constants of substitutients were taken from Ref. [17].



Figure 1. CV of 1-naphthonitrile (**7**) at scan rates of 0.10 V/s: reduction (a) and oxidation (b)

tory linear correlation (r = 0.978) between the values of the first reduction peak potentials of 1-X-naphthalenes (X = H, CHO, COCH₃, CO₂CH₃, COPh, CN, NO₂) and corresponding benzene derivatives points to the uniformity of substituent influences on the reduction potentials in these two series of compounds.

As follows from the ν values at which the peak of the RA oxidation (peak 1A) to appear, the most stable are the RAs of 1-X-naphthalenes with X = NO₂, CN, COPh, COCH₃ and CO₂CH₃. In all these cases, the peak 1A is intensive at $\nu = 0.02$ V/s. For the compounds with X = CH₃, OCH₃ and CONH₂, it appears at $\nu = 0.1$ V/s, and for naphthalene itself – at $\nu = 0.05$ V/s. The least stable is the RA with X = CON(CH₃)₂: in this case peak 1A appears only at $\nu = 2$ V/s, though, apparently, this electron-accepting group should stabilize a RA more effectively, than the electron-donating methyl and methoxy groups.

Upon reduction of **10** in CH₃CN, the distinctly discerned peak 1A appears at the $\nu = 0.2$ V/s, and in DMF – at $\nu < 0.01$ V/s, that testifies to greater stability of the RA in the latter case. Unlike this, transition from CH₃CN to DMF does practically not affect the stability of the RA of **6**.

The second reduction peak (peak 2C), admittedly attributed to the reduction of a RA to a dianion, was observed in cases of $X = NO_2$, COPh, COCH₃ and also CHO in DMF (Table 1). For all substances, the second reduction peak is irreversible with all

studied sweep rates that testifies to instability of corresponding dianions.

The experimental values of peak 1C potentials of 1-X-naphthalenes correlate well with their DFT BLYP calculated LUMO energies (r = 0.986) and adiabatic electron affinities (r = 0.980) (EA_{ad} = $E_N - E_{RA}$, where E_N and E_{RA} – full energies of neutral 1-X-naphthalene and its RA, accordingly) listed in Table 1. This probably means that the molecular structures of 1-X-naphthalenes 1–11 and their RAs calculated with DFT BLYP are close to that in solution, and the influence of solvation on the energy of one-electron reduction is insignificant.

1-X-Naphthalene RAs stable under CV conditions have been electrochemically generated at the peak 1C potential in the resonator of an ESR spectrometer (for example Fig. 2). The experimental hyperfine interaction (hfi) constants and the $\tau_{1/2}$ values of RAs, along with DFT BLYP calculated hfi constants and the respective literature data for RAs of **1**, **2**, **7**, **11** are shown in Table 2.

In DMF at 295 K, the most long-lived are RAs of 1-X-naphthalenes **7** (X = CN, $\tau_{1/2} = 729$ s) and **11** (X = NO₂, $\tau_{1/2} = 213$ s). The RAs with X = CH₃, COOCH₃, COPh, COCH₃ are somewhat less stable ($\tau_{1/2} = 70-130$ s). Even less stable is a RA of **10** (X = CHO, $\tau_{1/2} = 30$ s), and a RA of **3** (X = OMe) was possible to be registered only at $T \le 253$ K as at higher temperature it is unstable. The RA of **5** (X = CONH₂) was unstable and undetectable by ESR even at 243 K. Since the sweep rate at which a anode peak 1A of **6** (X = CON(CH₃)₂) in the reverse part of reduction CV becomes observable much more, than that for RA of **5** ($\nu^{rev} \ge 2$ V/s), there was no point to generate electrochemically AR of **6**. As a whole, the data obtained are in line with the above CV estimation of the RA relative stability in CH₃CN.

The experimental hfi constants (*a*) of 1-X-naphthalene RAs were assigned on the basis of comparison with the corresponding values calculated by the DFT BLYP method with full geometry optimization. There is a good correspondence between the experimentally obtained and calculated hfi constants. An exception is the discrepancy between the experimental and calculated a_N values for the RA of 1-nitronaphthalene, the first value being ~4 times larger than the second one. This fact may be due to the underestimation of the exchange interactions for the planar π -radicals with the spin-polarization mechanism of the isotropic hyperfine coupling on ¹⁴N nucleus.^[18] Nevertheless, the assignment of this constant in the ESR spectrum is unambiguous due to a characteristic 1:1:1 triplet due to coupling with ¹⁴N nucleus.

According to the DFT BLYP results, the naphthalene fragment in a RAs is flat, the substituents $X = NO_2$, CHO, COCH₃, COPh, CO_2CH_3 are in co-planarity with it thus promoting a negative charge and spin density delocalization. The C=O bond of substituents X = CHO, COCH₃, COPh, CO_2CH_3 is transoid to the naphthalene C^1 — C^2 bond. In the RAs with $X = CONH_2$ and CON(CH₃)₂, the carbonyl group also is aside to a non-substituded ring, in so doing the amide group being out-of-plane deviated by 10° and 20° , respectively.

For naphthalene **1** RA, $a(H^{\alpha})/a(H^{\beta}) = 2.6$ (Table 2). An electronwithdrawing substituent in the naphthalene position 1 disperses a part of RA spin density and redistributes it inside a naphthalene framework. So, substituents X = CHO, $COCH_3$, $COOCH_3$, CNincrease $a(H^2)$ 2.5–3 times and $a(H^4) \sim 1.5$ times ($a(H^4)$ in RA of **11** is increased only slightly). In contrast, the $a(H^3)$ constants in the specified RAs are 2.8–4.7 times decreased as compared to the naphthalene RA.



Figure 2. Experimental (a) and simulated (b) ESR spectra of RAs from electrochemical reduction of 1-X-naphthalenes 3, 4, 9 in DMF

As a whole, for the non-substituted naphthalene fragment of RAs with substantially electron-accepting X substituents the tendency is observed to distinctly decrease the a(H) values as compared with the naphthalene RA. The hfi constant $a(H^5)$ in RAs of **7** (X = CN), **4**, **9**, **10** (X = CO₂CH₃, COCH₃, CHO) and **11** (X = NO₂) is 1.5–3 times decreased. The ratios of $a(H^8)$ and $a(H^6)$ values in RA of **1** to $a(H^8)$ and $a(H^6)$ in its 1-X-substituted derivatives depend on the nature of X more specifically, being raised from ~2–3.4 for RAs of **7** and **11** up to ~7 for $a(H^8)$ in RAs of **4**, **9**, **10** and to 17 for $a(H^6)$ in RA of **9**. At the same time, the influence of electron-accepting substituents on the $a(H^7)$ value is slight and ambiguous: in RA of **7** (X = CN) it is practically the same, in RA of **11**

 $(X=NO_2)$ ${\sim}1.3$ times reduced and in RAs of 4, 9, 10 (X = CO_2CH_3, COCH_3, CHO) ${\sim}1.3$ times increased as compared to naphthalene RA.

Unlike electron-accepting substituents, electron-donating ones influence on hfi constants more moderately: methyl and methoxy groups in the naphthalene position 1 render $a(H^5)$ and $a(H^8)$ 5–20% larger and $a(H^4)$ 20–30% smaller.

Some conclusions about the influence of the nature of substituent X on the distribution of unpaired electron density (UED) in RAs of 1-substituted naphthalenes could be done on the basis of hfi constants presented in Table 2. The UED in RAs with electron-donating substituents CH_3 and OCH_3 , such as in the

Table 2. Experimental and calculated hfi constants of ESR spectra of 1-X naphthalene (1–4, 7–11) RAs and their half-life times $\tau_{1/2}$ (T = 295 K)

R	$ au_{1/2}$, s	hfi constants, mT	
н	—	Lit. ⁷ : H1, H4, H5, H8 0.479; H2, H3, H6, H7 0.184	
CH₃	69	Lit. ⁸ ^a : H2 0.153; H3 0.223; H4 0.416; H5 0.549; H6 0.149; H7 0.196; H8 0.523; H (CH ₃) 0.361 DFT BLYP: H2 0.166; H3 0.196; H4 0.490; H5 0.542; H6 0.136; H7 0.244; H8 0.513; H (CH ₃) 0.406	
OCH₃	379	Experimental: H2 0.157; H3 0.194; H4 0.432; H5 0.530; H6 0.135; H7 0.231; H8 0.497; H (CH_3) 0.578 DFT BLYP: H2 0.186; H3 0.170; H4 0.485; H5 0.529; H6 0.196; H7 0.192; H8 0.547; H (CH_3) 0.023	
CO₂Me	(243 K) 120	Experimental: H2 0.179; H3 0.128; H4 0.370; H5 0.546; H6 0.208; H7 0.184; H8 0.587; H (OCH ₃) 0.010 DFT BLYP: H2 0.439; H3 0.034; H4 0.684; H5 0.280; H6 0.018; H7 0.214; H8 0.152; H (CH ₃) 0.078	
CN	729	Experimental: H2 0.514; H3 0.038; H4 0.792; H5 0.271; H6 0.012; H7 0.237; H8 0.077; H (CH ₃) 0.062 Lit. ⁹ : H2 0.227; H3 0.042; H4 0.785; H5 0.465; H6 $<$ 0.008; H7 0.170; H8 0.308; N (CN) 0.128 DFT BLYP: H2 0.376; H3 0.081; H4 0.678; H5 0.348; H6 0.076; H7 0.211; H8 0.266; N (CN) 0.088	
COPh	132	Experimental: H2 0.444; H3 0.047; H4 0.770; H5 0.313; H6 0.015; H7 0.180; H8 0.225; N (CN) 0.122 Unresolved specter	
COMe	99	DFT BLYP: H2 0.401; H3 0.028; H4 0.663; H5 0.251; H6 0.056; H7 0.217; H8 0.099; H (CH ₃) 0.304 Experimental: H2 0.512; H3 0.039; H4 0.757; H5 0.235; H6 0.017; H7 0.229; H8 0.070; H (CH ₃) 0.337	
СНО	30	DFT BLYP: H2 0.380; H3 0.047; H4 0.677; H5 0.262; H6 0.008; H7 0.226; H8 0.106; H (CHO) 0.450 Experimental: H2 0.508; H3 0.057; H4 0.791; H5 0.246; H6 0.011; H7 0.237; H8 0.065; H (CHO) 0.525	
NO ₂	213	Lit. ⁹ H2 0.544; H3 0.062; H4 0.552; H5 0.165; H6 0.070; H7 0.141; H8 0.137; N (NO ₂) 0.772 DFT BLYP: H2 0.412; H3 0.013; H4 0.545; H5 0.200; H6 0.014; H7 0.181; H8 0.062; N (NO ₂) 0.191 Experimental: H2 0.541; H3 0.065; H4 0.549; H5 0.166; H6 0.065; H7 0.140; H8 0.140; N (NO ₂) 0.756	
^a Reduction with Na in THF.			

naphthalene RA, is located mainly in α -positions of the naphthalene nucleus. In so doing, it is a little bit larger in positions 5 and 8 and a little bit smaller in position 4 as compared with the respective positions in the naphthalene RA, that testifies to forcing out a small part of UED from an X-substituted ring into a non-substituted ring. In contrast, introduction of electronaccepting substituents draw up UED into the substituted ring along with the redistribution of UED between positions 2 and 4 in favour of the first, the redistribution being the larger with the substituent X is more electron accepting: the ratio $a(H^4)/a(H^2)$ is 1.73 for RA of **7** (X = CN), \sim 1.5 for RA of **4**, **9**, **10** (X = COR) and \sim 1 for RA of $11 (X = NO_2)$. The similar UED redistribution is characteristic of an unsubstituted ring: in going from naphthalene RA to RAs of 4, 7-11 the UED in position 7 increases relatively those in positions 5 and, especially, 8. The overall pattern of UED redistribution as depending on a nature of X substituent demonstrates two types of unpaired electron MOs in the RAs under consideration: the first is characteristic for RAs of unsubstituted naphthalene and its derivatives with electron-donating substituents X, the second is mainly due to the resonance conjugation of electron-withdrawing substituent X with positions 2, 4, 5 and 8 of naphthalene nucleus.

Ring positions in RA, bearing a significant spin density, are the potential sites of radical recombination, including dimerization. So, according to data,^[19] dimerization of a 1-naphthonitrile RA occurs at the position *para* to the CN group. Hence, one can believe, that diverse radical reactions of 1-X-naphthalene RAs with electron-accepting X will exhibit the same regiochemistry.

Besides reduction potentials, oxidation potentials of 1-X-naphthalenes have also been measured with the use of the CV method and oxidation peaks for all compounds under investigation have been registered in an accessible potential range. The value of the first oxidation peak potential varies with substituent X from 1.33 V (X = OCH₃) to 2.13 V (X = NO₂). The influence of X nature is well consistent with its electronic effect which is illustrated by a good linear correlation between E_p^{1Ox} values and substituent σ_{p-X} – constants (r = 0.982), the points of the electron-donating substituents fit to this correlation only with electrophilic σ_p^+ constants. The first oxidation peaks are diffusionally controlled and for the most of compounds investigated correspond to transfer of two or more electrons ($l_p^{1Ox} \ge 2.8 \ l_p^{1C}$). Reversible oxidation peaks of 1-X-naphthalenes including those with electron-donating substituents could not been observed even at high electrode polarization rate (v = 50–100 V/s). Thus, 1-X-naphthalene radical cations are



Figure 3. Comparison of the electrochemical oxidation and reduction potentials of 1-X-naphthalenes

extremely unstable and rapidly undergo subsequent reactions (the fast ECE process), where the second and subsequent electrons are transferred from the products. Unfortunately, one cannot compare the values obtained of 1-X-naphthalene oxidation potential with similar data for corresponding benzene

electron-accepting substituents. There are satisfactory linear correlations between oxidation and reduction potentials of the compounds under investigation (Fig. 3), different for compounds with electron-accepting and with electron-donating substituents. So the E_p^{1C} values are more sensitive to the nature of the electron-accepting substituent, whereas the E_p^{10x} – to the nature of the electron-donating substituent. The only point not obeying the linear relationship is that of 1-naphthonitrile which is likely due to its reduction potential (*vide supra*).

derivatives because of the lack of such data for benzenes with

CONCLUSIONS

Thus, electrochemical reduction and oxidation potentials of a series of 1-substituted naphthalenes have been measured by the CV method in unified conditions. The first reduction peak of the most of compounds investigated has been established to be due to a one-electron transfer to form respective stable RAs. For the first time, their ESR spectra have been registered and interpreted, and also their half-life times have been estimated. Unlike that of electrochemical reduction, the first stage of electrochemical oxidation of 1-substituted naphthalenes has been revealed to be irreversible and corresponding to a multiple electron transfer.

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