Electrochemical Reduction of Organic and Organometallic Compounds. Polarization Effect in Radical Anions

O. V. Novikova, O. V. Kuznetsova, and A. N. Egorochkin
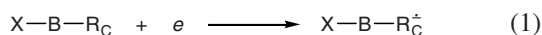
Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
ul. Tropinina 49, Nizhnii Novgorod, 603950 Russia
e-mail: egor@iomc.ras.ru

Abstract—Half-wave potentials of electrochemical reduction and electron affinities of $X–B–R_C$ compounds belonging to 23 reaction series depend not only on the inductive and resonance effects but also on the polarization effect of the X substituent, which was not taken into account previously. In some cases, the contribution of the polarization effect reaches 50% of the overall substituent effect. The main factors responsible for the magnitude of polarization effect in $X–B–R_C^{\div}$ radical anions are the natures of reaction center R_C and bridging moiety B and the distance between the substituent X and reaction center R_C.

DOI: 10.1134/S1070428007090023

Substituent effects on half-wave potentials $E_{1/2}$ of electrochemical reduction of organic compounds were the subjects of numerous studies (see, e.g., [1–6]). As a rule, electrode processes like (1) are considered while studying effects of substituents X on $E_{1/2}$:

$$X—B—R_C + e \longrightarrow X—B—R_C^{\div} \qquad (1)$$

Here, $X–B–R_C$ is a compound belonging to a reaction series, where R_C is the reaction center (an electrochemically active group, which is the same for all compounds of that series), X is a substituent affecting reaction (1) but not participating in it directly, and B is a bridging group connecting R_C and X.

Reactions (1) in solution involve electron transfer to the lowest unoccupied molecular orbital (LUMO). The half-wave potential $E_{1/2}$ is a relative measure of the LUMO energy E_{LUMO}. Electrochemical reactions like (1) may be reversible and irreversible. In reversible processes, the half-wave potential $E_{1/2}$ is proportional to the Gibbs energy $\Delta G°$. If a process is irreversible (provided that the reaction mechanism does not change within a reaction series), $E_{1/2}$ is proportional to the Gibbs energy of activation $\Delta G^{\neq}$. This means that both reversible and irreversible electrochemical reduction processes conform to the linear free energy relationship (LFER) principle (for details, see [2]).

As follows from the LFER principle and the postulate implying independence and additivity of different substituent effects, the half-wave potentials $E_{1/2}$ for an $X–B–R_C$ series (R_C = const) fit general relation (2):

$$E_{1/2} = E_{1/2}^{H} + a\sigma_I + b\sigma_R^{-}(\sigma_R) + \text{other terms.} \qquad (2)$$

Here, $E_{1/2}^{H}$ is the $E_{1/2}$ value for X = H; σ_I is a universal inductive constant of substituent X; σ_R^{-} and σ_R are constants characterizing resonance effect of substituent X when the reaction center R_C has, respectively, a large or small negative charge q^{-}; and a and b are coefficients. Let us consider factors giving rise to appearance of other terms in Eq. (2). For this purpose, so-called classical and nonclassical charged systems $X–B–R_C^{\div}$ should be examined. Classical systems in correlation analysis are *para*-substituted benzene derivatives $4\text{-}XC_6H_4R_C^{\div}$. In these systems ($R_C$ = const) the effect of group X is confined to inductive and resonance effects, and Eq. (2) is transformed into Eq. (3):

$$E_{1/2} = E_{1/2}^{H} + a\sigma_I + b\sigma_R^{-}(\sigma_R). \qquad (3)$$

Equation (3) is rigorously fulfilled only when resonance interaction between X and $R_C^{\div}$ (direct polar conjugation) in the $4\text{-}XC_6H_4R_C^{\div}$ system is absent.

The distance between X and R_C in nonclassical charged systems $X–B–R_C^{\div}$ (B = CH=CH, C≡C, etc.) and $X–R_C^{\div}$ is shorter than in classical ones. The small size of bridging group B or its absence is responsible for the appearance in nonclassical charged systems of

polarization effect which is untypical of classical systems. The presence of a positive or negative charge q on the reaction center R_C in nonclassical systems $X–B–R_C^q$ and $X–R_C^q$ leads to polarization of the X substituent, inducing a dipole. In terms of electrostatics [7], the energy E_{es} of ion–dipole interaction as a measure of polarization effect is expressed by Eq. (4):

$$E_{es} = -q^2\alpha/(2r^4). \qquad (4)$$

Here, q is the charge on the reaction center R_C, α is the polarizability of substituent X, and r is the distance between the charged center and induced dipole. Taking into account the power of r in Eq. (4), the energy E_{es} strongly depends on the distance r. Therefore, in classical systems $4\text{-}XC_6H_4R_C^q$ characterized by a long distance r polarization effect is likely to be absent or negligible. In nonclassical charged systems, the contribution of polarization effect is comparable with those of inductive and resonance substituent effects. It was estimated by correlation analysis performed for various radical cations XR_C^+ [8, 9] and $X_nR_C^{q+}$ systems as components of H-complexes [9] and donor–acceptor complexes [10]. For these positively charged systems, expressions like (5) are fulfilled:

$$P = P^H + a\sigma_I + b\sigma_R^+(\sigma_R) + c\sigma_\alpha. \qquad (5)$$

Here, P is a parameter such as ionization potential, frequency shift in the IR spectrum of H-complex, enthalpy, dipole moment of donor–acceptor complex, etc.); P^H is the value of P for X = H; σ_R^+ and σ_R are constants characterizing resonance effect of substituents X in systems with large and small positive charges on the reaction center R_C, respectively; and σ_α is the polarization constant of substituent X, which quantitatively characterizes its polarization effect. The values of σ_α for a large number of substituents X were calculated by nonempirical quantum-chemical methods [11]. The use of constants σ_α in correlation analysis makes it possible to avoid laborious calculations by formula (4).

As far as we know, polarization effect was not taken into account previously while studying the effect of substituents on the half-wave electrochemical reduction potentials $E_{1/2}$. Therefore, the goal of the present work was to examine general relations holding in electrochemical reduction of nonclassical systems with regard to polarization effect. We presumed that, as applied to nonclassical systems, general equation (2) should be rewritten as

$$E_{1/2} = E_{1/2}^H + a\sigma_I + b\sigma_R^-(\sigma_R) + c\sigma_\alpha. \qquad (6)$$

Then, the existence of polarization effect within a reaction series may be judged by improvement of statistical parameters in going from Eq. (3) to (6). It is clear that such an improvement may be achieved only when the σ_α term in Eq. (6) is statistically significant.

We analyzed the effect of substituents X on the half-wave potentials $E_{1/2}$ of electrochemical reduction and electron affinities EA of compound series *I–XXIII* with various reaction centers R_C (Tables 1–5). In each series, the LUMO that takes up an electron according to reaction (1) is localized mainly on R_C. In series *I, II,* and *X*, $R_C = C_6H_5$, and the LUMO is a π^*-orbital [5, 13, 19, 20, 29]. Series *V–VII* ($R_C = CHlg$) are characterized by $\sigma^*(CHlg)$-type LUMOs [5, 14–17, 20]. The LUMOs in compounds of series *III* and *IV* are likely to belong to a mixed π^*,σ^*-type. The degree of mixing depends on the nature of X. If X = H or A (where A is a resonance acceptor group like CN, CHO, CF_3, etc.; Table 1), the LUMO is contributed mostly by π^*-orbitals [5, 12, 13, 29]. If X = D (where D is a resonance donor such as NH_2 or OMe group; Table 1), the σ^* contribution increases [5, 17, 20, 29]; however, it is unlikely that the reaction center R_C in radical anions $1,4\text{-}DC_6H_4Hlg^{\cdot-}$ (Hlg = Cl, Br) is the C–Hlg bond.

It is known [30] that the substituents D and A in *para*-substituted benzene derivatives like $1,4\text{-}DC_6H_4A$ interact with each other according to the direct polar conjugation mechanism. Therefore, the effects of substituents like D and A in series *II–V* should be considered separately (Table 6).

The reaction center R_C in series *VIII* is the =CH–carbon atom, and the LUMO is a π^*-orbital [6]. The reaction center R_C in series *IX* is likely to reside on the mercury atom [18]. In disulfides *XI*, $R_C = S–S$, and the LUMO is of $\sigma^*(S–S)$ type [20, 21]. The reaction center R_C in series *XII–XXIII* compounds is localized mainly on the transition metal atom, and the LUMO is contributed by the metal orbitals and partially by the ligand orbitals [20].

The parameters of Eqs. (3) and (6) for series *I–XXIII* (Table 6) were calculated using standard Statgraphics 3.0 software (least-squares procedure, confidence probability 95%) on the basis of standard values of substituent constants σ_I, σ_R^-, σ_R, and σ_α (Table 7). First of all, let us consider briefly known [13] relations (7) and (8):

$$E_{1/2}(XBR_C) = -\Delta G°(XBR_C) - \delta\Delta G_{solv}°(XBR_C^{\cdot-}) + \text{const}; \qquad (7)$$

$$\delta\Delta G_{solv}°(XBR_C^{\cdot-}) = \Delta G_{solv}°(XBR_C^{\cdot-}) - \Delta G_{solv}°(XBR_C). \qquad (8)$$

Table 1. Half-wave potentials of electrochemical reduction ($-E_{1/2}$, V)[a] and electron affinities (EA, eV)[b] of series *I–V* compounds

Substituent X		C_6H_5X (*I*)	1,4-$XC_6H_4NO_2$ (*II*)	1,4-XC_6H_4Cl (*III*)	1,4-XC_6H_4Br (*IV*)	1,4-XC_6H_4I (*V*)
Resonance donors D	Me	–	1.17 (0.89)	–2.66	–2.34	–1.73
	NH_2	–	1.37	–	–2.47	–1.85
	NMe_2	–	1.35	–	–2.47	–1.85
	OMe	–	1.23 (0.85)	–2.65	–2.34	–1.75
	F	–	1.10 (1.05)	–	–	–
	Cl	–	1.02 (1.19)	–2.35	–2.11	–1.56
	Br	–	1.03 (1.29)	–2.11	–	–1.58
	H	–3.40	1.11 (0.97)	–2.63	–2.31	–1.71
Resonance acceptors A	NO_2	–1.11	0.57 (1.89)	–	–	–
	CN	–	0.79 (1.65)	–1.86	–1.76	–
	CHO	–1.80	0.78 (1.67)	–1.70	–	–1.46
	COMe	–1.99	(–1.31)	–1.77	–1.65	–1.54
	COPh	–	–	–	–	–1.46
	COOH	–2.12	0.80	–1.95	–1.86	–
	COOEt	–	0.89	–	–	–
	CF_3	–2.49	0.89 (1.47)	–	–2.03	–1.51

[a] Data of [5]; mercury electrode, solvent DMF.
[b] Data of [12, 13] are given in parentheses.

Table 2. Half-wave potentials of electrochemical reduction ($E_{1/2}$, V),[a] electron affinities (EA, eV), and LUMO energies (E_{LUMO}, eV) of series *VI–XI* compounds

Substituent X	X–Cl (*VI*) [14, 15]	X–Br (*VII*) [15–17]	XOC–CH=CH–Ph (*VIII*) [6]		$XHgClO_4$ (*IX*) [18]	XSPh (*X*) [19, 20]	XSSX (*XI*) [21][b]
	$-EA$	$-EA$	$-E_{1/2}$	$-E_{LUMO}$	$-E_{1/2}$	$-E_{1/2}$	$-E_{1/2}$
Me	3.45	2.4	1.64	2.347	0.612	2.751	–
Et	2.35	1.26	–	–	0.594	2.734	1.78
Pr	2.4	1.20	–	–	0.613	–	1.80
i-Pr	1.99	–	–	–	–	2.703	1.80
Bu	2.39	–	–	–	–	–	1.80
t-Bu	1.80	–	1.68	2.267	–	2.638	2.0
C_5H_{11}	–	–	–	–	0.535	–	–
Ph	–	2.0	1.41	2.542	0.544	2.549	1.65
CH_2Ph	–	–	–	–	0.370	2.569	1.42
$CH_2CH=CH_2$	–	–	–	–	–	2.655	–
CH_2CN	–	–	–	–	–	2.351	–
OMe	–	–	1.81	2.172	–	–	–
H	–	–	1.53	2.516	–	–	–
CN	–	–	0.83	3.389	–	–	–
CF_3	3.0	0.82	–	–	–	–	–

[a] Mercury electrode; solvent DMF.
[b] Solvent MeOH–*i*-PrOH–H_2O.

Table 3. Half-wave potentials of electrochemical reduction ($-E_{1/2}$, V)[a] of series *XII–XV* compounds

Substituent X	Series (series no.)			
	$XW(\eta^5\text{-}C_6H_5)(CO)_3$ (*XII*) [22]	$XRh(CO)(PPh_3)_2$ (*XIII*) [23]	$XIr(CO)(PPh_3)_2$ (*XIV*) [23]	$1,4\text{-}XC_6H_4Rh(CO)(PPh_3)_2$ (*XV*) [24][b]
Me	2.00	–	–	2.58
Ph	1.89	–	–	–
OH	–	2.45	2.68	–
OMe	–	–	–	2.59
SPh	–	2.10	2.22	–
F	–	2.34	2.55	–
Cl	0.82	2.05	2.22	2.47
Br	0.73	2.00	2.07	–
H	–	–	–	2.53
N_3	–	2.12	2.23	–
NO_2	–	1.80	1.88	–
CN	1.45	–	–	–
CF_3	–	–	–	2.45

[a] Mercury electrode; solvent acetonitrile.
[b] Solvent $MeCN\text{–}C_6H_6$.

Table 4. Half-wave potentials of electrochemical reduction ($-E_{1/2}$, V)[a] of series *XVI–XVIII* compounds

Substituent X_3	Series (series no.)		
	$(X_3P)Co(\eta^3\text{-}C_3H_5)(CO)_2$ (*XVI*) [25]	$(X_3P)_2Rh(CO)Cl$ (*XVII*) [26]	$cis\text{-}(X_3P)_2PtCl_2$ (*XVIII*) [27][b]
Me_3	–	3.02	1.70
Et_3	–	3.00	2.05
Bu_3	2.174	–	–
Me_2, Ph	–	2.83	–
Me, Ph_2	–	–	1.67
Pr, Ph_2	–	–	1.75
C_5H_{11}, Ph_2	–	–	1.72
Ph_3	1.962	2.43	1.60
$(NMe_2)_3$	–	2.70	–
$(OMe)_3$	1.934	–	–
$(OEt)_3$	2.098	–	–
$(OPh)_3$	1.836	–	–

[a] Mercury electrode; solvent acetonitrile.
[b] Gold amalgam electrode.

Here, $E_{1/2}(XBR_C)$ are the half-wave reduction potentials of compounds belonging to $X\text{–}B\text{–}R_C$ series [reaction (1) in solution]; $\Delta G°(XBR_C)$ is the Gibbs energy of gas-phase reaction (1); $\delta\Delta G°_{solv}(XBR_C^{\ \cdot -})$ is the difference in the Gibbs energies of solvation of radical anions $X\text{–}B\text{–}R_C^{\ \cdot -}$ and the corresponding neutral molecules $X\text{–}B\text{–}R_C$; and the value of const is determined by the conditions of process (1).

Equation (7) can be simplified on the basis of two assumptions [13]. First, electron affinity is given by Eq. 9 (by definition):

$$EA(XBR_C) = -\Delta H°(XBR_C), \qquad (9)$$

where $\Delta H°(XBR_C)$ is the enthalpy of reaction (1). In the Gibbs–Helmholtz equation (10) for gas-phase

process (1), the entropy contribution $T\Delta S°(\mathrm{XBR_C})$ to the free energy $\Delta G°(\mathrm{XBR_C})$ is as small as several percents [13]:

$$\Delta G°(\mathrm{XBR_C}) = \Delta H°(\mathrm{XBR_C}) - T\Delta S°(\mathrm{XBR_C}). \quad (10)$$

Therefore, Eq. (9) is well approximated by Eq. (11):

$$EA(\mathrm{XBR_C}) = -\Delta G°(\mathrm{XBR_C}). \quad (11)$$

In particular, from Eq. (11) it follows that electron affinity conforms to the LFER principle.

Second, the value of $\Delta G°_{\mathrm{solv}}(\mathrm{XBR_C^{\cdot-}})$ in Eq. (8) is larger than $\Delta G°_{\mathrm{solv}}(\mathrm{XBR_C})$, for radical anion is solvated to a stronger extent than neutral molecule. Furthermore, as shown in [13], $\Delta G°_{\mathrm{solv}}(\mathrm{XBR_C^{\cdot-}})$ is approximately constant within a single reaction series $\mathrm{X-B-R_C}$ ($\mathrm{R_C} = \mathrm{const}$), i.e., it does not depend on the nature of the X substituent. Therefore, Eq. (7) is transformed into (12):

$$E_{1/2}(\mathrm{XBR_C}) = EA(\mathrm{XBR_C}) + \mathrm{const}. \quad (12)$$

The validity of Eq. (12) is confirmed by both published data [2, 13] and correlation (13) obtained by us for series *II*.

$$E_{1/2}(II) = (0.56\pm0.04)EA(II) - (1.69\pm0.05); \quad (13)$$
$$S_Y = 0.04, R = 0.985, n = 10.$$

Here, $E_{1/2}(II)$ and $EA(II)$ are the half-wave potentials and electron affinities, respectively, of series *II*

compounds. In terms of the rough Koopmans approximation [13, 30], electron affinity *EA* is related to the LUMO energy E_{LUMO} through simple expression (14):

$$EA = -E_{\mathrm{LUMO}}. \quad (14)$$

Therefore, a linear relation between $E_{1/2}$ and E_{LUMO} may be expected. Such relation for series *VIII* compounds looks as follows:

$$E_{1/2}(VIII) = -(0.78+0.04)E_{\mathrm{LUMO}} - (3.48+0.12); \quad (15)$$
$$S_Y = 0.04, R = 0.993, n = 6.$$

Thus Eqs. (12)–(15) indicate the existence of a close relation between processes like (1) occurring in solution and in the gas phase.

Comparison of Eqs. like (3) and (6) (Table 6) reveals an important specificity of substituent effects in charged nonclassical systems $\mathrm{X-B-R_C^{\cdot-}}$ and $\mathrm{X-R_C^{\cdot-}}$, which remained beyond attention so far; this specificity is polarization effect. As follows from the data in Table 6, statistical parameters are improved in going from Eq. (3) to (6): standard errors of approximation S_Y become smaller, and correlation coefficients R increase. Therefore, we can state with certainty that polarization effect of substituents in charged nonclassical radical anions $\mathrm{X-B-R_C^{\cdot-}}$ and $\mathrm{X-R_C^{\cdot-}}$ is significant. Characteristically, compounds of classical series *XV* and *XXI* lack polarization effect.

Let us consider some specific features of the polarization effect. For this purpose, we rewrite Eq. (6)

Table 5. Half-wave potentials of electrochemical reduction $(-E_{1/2}, \mathrm{V})^a$ of series *XIX–XXIII* compounds

Substituent X	Series (series no.)				
	$[\mathrm{X_2C_2S_2}]_3\mathrm{W}$ (*XIX*)[b]	$[\mathrm{X_2C_2S_2}]_2\mathrm{Ni}$ (*XX*)[b]	$[(4\text{-}\mathrm{XC_6H_4})_2\mathrm{C_2S_2}]_2\mathrm{Ni}$ (*XXI*)[b]	$[\mathrm{X_2C_2S_2}]_2\mathrm{Pd}$ (*XXII*)	$[\mathrm{X_2C_2S_2}]_2\mathrm{Pt}$ (*XXIII*)
Me	–0.333 (–0.994)	–0.107 (–1.117)	0.083 (–0.960)	–0.06	–0.133
Et	–	–0.119 (–1.138)	–	–	–
Pr	–	–0.121 (–1.154)	–	–	–
i-Pr	–	–0.151 (–1.204)	–	–	–
Ph	–0.041 (–0.684)	0.134 (–0.881)	–	0.182	0.090
$\mathrm{C_6H_4Me}$-*p*	–0.091 (–0.681)	–	–	–	0.043
OMe	–	–	0.035 (–0.945)	–	–
Cl	–	–	0.218 (–0.757)	–	–
H	–0.133 (–0.845)	0.120 (–0.921)	0.134 (–0.881)	0.165	–
CN	–	1.049 (–0.259)	–	0.473	0.243
$\mathrm{CF_3}$	0.91 (0.35)	1.030 (–0.088)	–	0.996	0.852

[a] Data of [28]; platinum electrode, solvent DMF.
[b] Given are $E_{1/2}$ values for two consecutive steps of the reduction process.

Table 6. Coefficients and their standard deviations ($P^H \pm S_R$, $a \pm S_a$, $b \pm S_b$, $c \pm S_c$) in the equations $P(E_{1/2}, EA) = (P^H \pm S_P) + (a \pm S_a)\Sigma\sigma_I + (b \pm S_b)\Sigma\sigma_R^-(\sigma_R) + (c \pm S_c)\Sigma\sigma_\alpha$, and $E_{1/2} = (E_{1/2}^H \pm S_E) + (a \pm S_a)\Sigma\sigma_p$, standard approximation errors S_Y, correlation coefficients R, and sample sizes n for series I–$XXIII$ compounds

Series no.	Parameter P	$P^H \pm S_P$	$a \pm S_a$	$b \pm S_b$	σ^a	$c \pm S_c$	S_Y^b	R^b	n
I	$E_{1/2}$	-3.43 ± 0.09	3.94 ± 0.28	-6.36 ± 1.22	σ_R	-2.09 ± 0.30	0.09 (0.37)	0.993 (0.875)	6
II^c	$E_{1/2}(D)$	-1.13 ± 0.02	0.34 ± 0.03	0.34 ± 0.03	σ_R	-0.05 ± 0.04	0.03 (0.03)	0.978 (0.977)	8
	$E_{1/2}(A)$	-1.10 ± 0.03	0.49 ± 0.10	0.47 ± 0.11	σ_R^-	0.32 ± 0.12	0.03 (0.05)	0.979 (0.946)	7
	$EA(D)$	0.98 ± 0.03	0.86 ± 0.08	0.69 ± 0.09	σ_R^-	-0.07 ± 0.06	0.03 (0.03)	0.983 (0.982)	6
	$EA(A)$	0.97 ± 0.01	1.32 ± 0.04	1.26 ± 0.04	σ_R^-	1.33 ± 0.06	0.01 (0.15)	0.999 (0.861)	5
III^c	$E_{1/2}(D)$	-2.65 ± 0.10	0.86 ± 0.350	0.59 ± 0.31	σ_R^-	-0.35 ± 0.31	0.10 (0.11)	0.905 (0.892)	5
	$E_{1/2}(A)$	-2.62 ± 0.04		0.80 ± 0.17	σ_R^-	-0.80 ± 0.21	0.04 (0.09)	0.995 (0.972)	5
IV^c	$E_{1/2}(D)$	-2.32 ± 0.02	0.47 ± 0.05	0.29 ± 0.02	σ_R	-0.14 ± 0.05	0.02 (0.03)	0.992 (0.972)	6
	$E_{1/2}(A)$	-2.31 ± 0.01	-0.18 ± 0.02	0.58 ± 0.04	σ_R^-	-0.77 ± 0.03	0.01 (0.05)	0.999 (0.982)	5
V^c	$E_{1/2}(D)$	-1.71 ± 0.01	0.32 ± 0.05	0.24 ± 0.02	σ_R	-0.09 ± 0.05	0.02 (0.02)	0.988 (0.978)	7
	$E_{1/2}(A)$	-1.71 ± 0.01	0.90 ± 0.11	-1.14 ± 0.24	σ_R	-0.13 ± 0.03	0.01 (0.04)	0.991 (0.917)	5
VI	EA	-6.47 ± 1.03	20.05 ± 9.64	-19.47 ± 10.10	σ_R^-	-4.43 ± 0.60	0.17 (0.64)	0.955 (0.000)	7
VII	EA	-1.92 ± 0.17	-8.63 ± 1.12	20.42 ± 2.17	σ_R	-4.46 ± 0.61	0.12 (0.61)	0.983 (0.335)	5
$VIII$	$E_{1/2}$	-1.53 ± 0.04	0.98 ± 0.08	1.03 ± 0.08	σ_R	-0.12 ± 0.06	0.04 (0.06)	0.993 (0.984)	6
IX	$E_{1/2}$	-0.891 ± 0.061	0	-1.28 ± 0.26	σ_R^-	-0.26 ± 0.09	0.032 (0.035)	0.938 (0.925)	6
X	$E_{1/2}$	-2.659 ± 0.057	0.673 ± 0.174	1.532 ± 0.322	σ_R	-0.296 ± 0.094	0.034 (0.057)	0.964 (0.898)	8
XI	$E_{1/2}$	-1.70 ± 0.13	7.86 ± 0.39	-2.99 ± 0.40	σ_R^-	0.25 ± 0.20	0.04 (0.05)	0.995 (0.994)	7
XII	$E_{1/2}$	-1.97 ± 0.06	2.32 ± 0.08	-2.49 ± 0.13	σ_R	0.64 ± 0.10	0.04 (0.16)	0.998 (0.962)	5
$XIII$	$E_{1/2}$	-2.50 ± 0.18	0.87 ± 0.29	0.40 ± 0.14	σ_R	-0.29 ± 0.08	0.04 (0.09)	0.980 (0.910)	7
XIV	$E_{1/2}$	-2.92 ± 0.21	1.34 ± 0.34	0.35 ± 0.16	σ_R	-0.46 ± 0.09	0.05 (0.14)	0.984 (0.865)	7
XV	$E_{1/2}$	-2.54 ± 0.01	0.19 ± 0.03	$-$	σ_P	$-$	0.02	0.970	5
XVI	$E_{1/2}$	-0.656 ± 0.428	0.881 ± 0.149	1.083 ± 0.276	σ_R^-	0.539 ± 0.166	0.028 (0.068)	0.978 (0.864)	5
$XVII$	$E_{1/2}$	-2.78 ± 0.02	0.85 ± 0.02	0.50 ± 0.02	σ_R^-	-0.08 ± 0.01	0.003 (0.021)	0.999 (0.996)	5
$XVIII$	$E_{1/2}$	-5.47 ± 1.21	-1.45 ± 0.92	-8.63 ± 2.18	σ_R	-0.42 ± 0.28	0.02 (0.03)	0.990 (0.986)	6
XIX^d	$E_{1/2}^1$	-0.133 ± 0.035	-3.768 ± 2.716	4.862 ± 3.109	σ_R^-	-1.172 ± 0.789	0.035 (0.045)	0.997 (0.996)	5
	$E_{1/2}^2$	-0.845 ± 0.002	-6.343 ± 0.163	7.865 ± 0.186	σ_R^-	-1.944 ± 0.047	0.002 (0.062)	1.000 (0.993)	5
XX^d	$E_{1/2}^1$	0.158 ± 0.043	0.791 ± 0.118	-0.228 ± 0.114	σ_R^-	0.138 ± 0.031	0.054 (0.118)	0.994 (0.973)	8
	$E_{1/2}^2$	-0.883 ± 0.045	0.959 ± 0.123	-0.492 ± 0.119	σ_R^-	0.186 ± 0.032	0.056 (0.154)	0.992 (0.934)	8
XXI^d	$E_{1/2}^1$	0.136 ± 0.003	0.089 ± 0.004	$-$	σ_P	$-$	0.006	0.998	4
	$E_{1/2}^2$	-0.864 ± 0.016	0.101 ± 0.021	$-$	σ_P	$-$	0.032	0.960	4
$XXII$	$E_{1/2}$	0.175 ± 0.015	1.635 ± 0.051	-1.188 ± 0.046	σ_R^-	0.385 ± 0.014	0.018 (0.359)	0.999 (0.471)	5
$XXIII$	$E_{1/2}$	0.127 ± 0.047	1.655 ± 0.096	-1.269 ± 0.085	σ_R^-	0.420 ± 0.026	0.033 (0.377)	0.996 (0.072)	5

[a] Resonance parameter in the $(b \pm S_b)\Sigma\sigma_R^-(\sigma_R)$ term.

[b] In parentheses are given the values of S_Y and R in correlation equations $P(E_{1/2}, EA) = (P^H \pm S_P) + (a \pm S_a)\Sigma\sigma_I + (b \pm S_b)\Sigma\sigma_R^-(\sigma_R)$, which were calculated with no account taken of polarization effect.

[c] $E_{1/2}(D)$ and $EA(D)$ correspond to equations calculated for compounds in which the substituent X is a resonance donor or hydrogen atom; $E_{1/2}(A)$ and $EA(A)$ correspond to equations calculated for compounds in which the substituent X is a resonance acceptor or hydrogen atom.

[d] $E_{1/2}^1$ and $E_{1/2}^2$ are half-wave potentials of the first and second stages of electrochemical reduction.

Table 7. Inductive σ_I, resonance σ_R and σ_R^-, and polarization constants σ_α of substituents X in series *I–XXIII* compounds[a,b]

Substituent X	σ_I	σ_R	σ_R^-	σ_α	Substituent X	σ_I	σ_R	σ_R^-	σ_α
H	0	0	0	0	OPh	0.37	–0.40	–0.47	–0.38
Me	–0.05	–0.12	–0.13	–0.35	SPh	0.30	–0.23	–0.12	–0.88
Et	–0.05	–0.10	–0.14	–0.49	F	0.45	–0.39	–0.48	0.13
Pr	–0.05	–0.10	–0.14	–0.54	Cl	0.42	–0.19	–0.23	–0.43
i-Pr	–0.03	–0.12	–0.12	–0.62	Br	0.45	–0.22	–0.20	–0.59
Bu	–0.05	–0.10	–0.14	–0.57	CN	0.51	0.15	0.49	–0.46
t-Bu	–0.07	–0.13	–0.14	–0.75	CH_2CN	0.17	0.01	–0.06	–0.55
C_5H_{11}	–0.05	–0.10	–0.14	–0.58	CHO	0.33	0.09	0.70	–0.46
Ph	0.12	–0.13	–0.10	–0.81	COMe	0.33	0.17	0.51	–0.55
$CH_2CH=CH_2$	–0.06	–0.08	–0.12	–0.57	COPh	0.31	0.12	0.52	–0.75
CH_2Ph	–0.04	–0.05	–0.26	–0.70	COOH	0.34	0.11	0.43	–0.34
NH_2	0.08	–0.74	–0.23	–0.16	COOEt	0.34	0.11	0.41	–0.34
NMe_2	0.15	–0.98	–0.27	–0.44	CF_3	0.38	0.16	0.27	–0.25
OH	0.33	–0.70	–0.70	–0.03	N_3	0.48	–0.40	–0.37	–0.49
OMe	0.29	–0.56	–0.55	–0.17	NO_2	0.65	0.13	0.62	–0.20
OEt	0.26	–0.50	–0.54	–0.23					

[a] Standard sets of substituent constants σ_I, σ_R, σ_R^-, and σ_α were taken from [8–11].
[b] $\sigma_R = \sigma_I + \sigma_R$.

Table 8. Inductive ($Ind = a\Sigma\sigma_I$), resonance ($Res = b\Sigma\sigma_R^-$ or $b\Sigma\sigma_R$), and polarization contributions ($Pol = c\Sigma\sigma_\alpha$) (%) to variation of parameters P ($E_{1/2}$, EA) induced by substituents X in series *I–XXIII* compounds

Series no.	Parameter P	Ind	Res	Pol	Series no.	Parameter P	Ind	Res	Pol
I	$E_{1/2}$	53±4	23±4	24±3	*XI*	$E_{1/2}$	73±4	23±3	4±3
II	$E_{1/2}(D)$	32±5	61±5	7±5	*XII*	$E_{1/2}$	52±2	37±2	11±2
	$E_{1/2}(A)$	40±8	40±10	20±7	*XIII*	$E_{1/2}$	33±11	36±13	31±9
	$EA(D)$	50±5	44±6	6±5	*XIV*	$E_{1/2}$	38±10	24±11	38±7
	$EA(A)$	29±1	39±1	32±1	*XV*	$E_{1/2}$	100		0
III	$E_{1/2}(D)$	45±18	33±18	22±19	*XVI*	$E_{1/2}$	31±5	40±10	29±9
	$E_{1/2}(A)$	0	56±12	44±12	*XVII*	$E_{1/2}$	58±1	30±1	12±2
IV	$E_{1/2}(D)$	39±4	50±4	11±4	*XVIII*	$E_{1/2}$	35±22	37±9	28±18
	$E_{1/2}(A)$	11±1	37±2	52±2	*XIX*	$E_{1/2}^1$	36±26	43±28	21±14
V	$E_{1/2}(D)$	36±6	53±4	11±7		$E_{1/2}^2$	37±1	42±1	21±1
	$E_{1/2}(A)$	57±7	30±6	16±4	*XX*	$E_{1/2}^1$	63±10	21±10	16±4
VI	EA	47±23	41±22	12±2		$E_{1/2}^2$	54±7	31±8	15±2
VII	EA	30±4	49±5	21±3	*XXI*	$E_{1/2}^1$	100		0
VIII	$E_{1/2}$	41±3	52±4	7±3		$E_{1/2}^2$	100		0
IX	$E_{1/2}$	0	63±13	37±13	*XXII*	$E_{1/2}$	47±2	37±2	16±1
X	$E_{1/2}$	32±8	42±9	26±8	*XXIII*	$E_{1/2}$	48±3	40±3	12±1

as (16), where P stands for $E_{1/2}$ or EA; P^H is the value of P for X = H; and $Ind = a\Sigma\sigma_I$, $Res = b\Sigma\sigma_R^-$ (or $b\Sigma\sigma_R$), and $Pol = c\Sigma\sigma_\alpha$ are, respectively, the contributions of inductive, resonance, and polarization effects to the total change of P by the action of substituent X:

$$P = P^H + Ind + Res + Pol. \qquad (16)$$

These contributions were calculated by the equations given in Table 6 and are collected in Table 8. It is seen that the polarization contributions Pol for classical series *XV* and *XXI* are equal to zero. Series *I–XIV*, *XVI–XX*, *XXII*, and *XXIII* are nonclassical. The distances r [see Eq. (4)] between X and R_C in compounds of these series are shorter than in compounds belonging to classical series, and the contribution Pol changes from 4 (series *XI*) to 52% (series *IV*). Generally speaking, the ratio of the *Ind*, *Res*, *Pol* contributions within a series depends on n, i.e., on the size and type of sample of substituents X (for details, see [9]). Therefore, let us consider only general trends in variation of *Pol*.

The contributions Pol to $E_{1/2}(A)$ and $EA(A)$ for series *II–IV* are larger than the corresponding contributions to $E_{1/2}(D)$ and $EA(D)$. The reason is at least two factors. The first of these is direct polar conjugation between *para*-substituents which strongly differ in their donor–acceptor properties. The second factor is participation of not only π^* but also σ^* orbitals in the formation of the LUMO in series *III* and *IV*. The first factor is likely to predominate in series *II*, while both factors are operative in series *III* and *IV*.

The reaction center R_C = C–I in series *V* compounds is remote from the substituent X (regardless of its nature) by a considerable distance r [Eq. (4)]. Therefore, the contributions Pol to $E_{1/2}(D)$ and $E_{1/2}(A)$ are fairly similar.

Polarization effect in transition metal derivatives is observed for radical anions X–$R_C^{\dot{-}}$ (R_C = Rh, Ir; series *XIII* and *XIV*) in which the substituent X is directly attached to the reaction center, as well for the fragments X–P–$R_C^{\dot{-}}$ (R_C = Co, Rh, Pt; series *XVI–XVIII*) and X–C=S–$R_C^{\dot{-}}$ (R_C = W, Ni, Pd, Pt; series *XIX*, *XX*, *XXII*, and *XXIII*). At R_C = const, the contribution Pol decreases as the distance r between X and $R_C^{\dot{-}}$ becomes longer [see Eq. (4)]. This is demonstrated by the data for rhodium (series *XIII*, *XVII*, and *XV*) and platinum derivatives (series *XVIII–XXIII*). The values of Pol for the first and second stages of electrochemical reduction of complexes with dithioketones (series *XIX–XXI*) are similar.

REFERENCES

1. Zuman, P., *Substituent Effects in Organic Polarography*, New York: Plenum, 1967.
2. Mairanovskii, S.G., Stradyn', Ya.P., and Bezuglyi, V.D., *Polyarografiya v organicheskoi khimii* (Polarography in Organic Chemistry), Leningrad: Khimiya, 1975.
3. Tomilov, A.P., Chernykh, I.N., and Kargin, Yu.M., *Elektrokhimiya elementoorganicheskikh soedinenii* (Electrochemistry of Organometallic Compounds), Moscow: Nauka, 1985.
4. Tomilov, A.P., Chernykh, I.N., and Kargin, Yu.M., *Elektrokhimiya elementoorganicheskikh soedinenii* (Electrochemistry of Organometallic Compounds), Moscow: Nauka, 1986.
5. Vasil'eva, N.V., Starichenko, V.F., and Shchegoleva, L.N., *Russ. J. Org. Chem.*, 1998, vol. 34, p. 1578.
6. Moraleda, D., El Abed, D., Pellissier, H., and Santelli, M., *J. Mol. Struct. (Theochem)*, 2006, vol. 760, p. 113.
7. Pacey, P.D. and Tan, Q.-T.N., *J. Phys. Chem.*, 1995, vol. 99, p. 17729.
8. Egorochkin, A.N. and Kuznetsova, O.V., *Russ. J. Org. Chem.*, 2005, vol. 41, p. 1407.
9. Egorochkin, A.N. and Kuznetsova, O.V., *Russ. J. Org. Chem.*, 2006, vol. 42, p. 175.
10. Kuznetsova, O.V., Egorochkin, A.N., and Novikova, O.V., *Russ. J. Gen. Chem.*, 2006, vol. 76, p. 554.
11. Hansch, C., Leo, A., and Taft, R.W., *Chem. Rev.*, 1991, vol. 91, p. 165.
12. Grimsrud, E.P., Caldwell, G., Chowdhury, S., and Kebarle, P., *J. Am. Chem. Soc.*, 1985, vol. 107, p. 4627.
13. Kebarle, P. and Chowdhury, S., *Chem. Rev.*, 1987, vol. 87, p. 513.
14. Guerra, M., Jones, D., Distefano, G., Scagnolari, F., and Modelli, A., *Chem. Phys.*, 1991, vol. 94, p. 484.
15. Underwood-Lemons, T., Winkler, D.C., Tossell, J.A., and Moore, J.H., *J. Chem. Phys.*, 1994, vol. 100, p. 9117.
16. Modelli, A., Scagnolari, F., Distefano, G., Jones, D., and Guerra, M., *J. Chem. Phys.*, 1992, vol. 96, p. 2061.
17. Olthoff, J.K., Tossell, J.A., and Moore, J.H., *J. Chem. Phys.*, 1985, vol. 83, p. 5627.
18. Butin, K.P., Beletskaya, I.P., Kashin, A.N., and Reutov, O.A., *J. Organomet. Chem.*, 1967, vol. 10, p. 197.
19. Gerdil, R., *J. Chem. Soc. B*, 1966, p. 1071.
20. Modelli, A., *Trends Chem. Phys.*, 1997, vol. 6, p. 57.
21. Hall, M.E., *Anal. Chem.*, 1953, vol. 25, p. 556.
22. Denisovich, L.I., Gubin, S.P., Chapovskii, Yu.A., and Ustynyuk, N.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1968, p. 924.
23. Schiavon, G., Zecchin, S., Pilloni, G., and Martelli, M., *J. Inorg. Nucl. Chem.*, 1977, vol. 39, p. 115.

24. Schiavon, G., Zecchin, S., Pilloni, G., and Martelli, M., *J. Organomet. Chem.*, 1976, vol. 121, p. 261.

25. Cardaci, G., Murgia, S., and Paliani, G., *J. Organomet. Chem.*, 1971, vol. 30, p. 253.

26. Montauzon, D. and de Poilblanc, R., *J. Organomet. Chem.*, 1975, vol. 93, p. 397.

27. Butin, K.P., Magdesieva, T.V., and Reutov, O.A., *Metalloorg. Khim.*, 1990, vol. 3, p. 534.

28. Olson, D.C., Mayweg, V.P., and Schrauzer, G.N., *J. Am. Chem. Soc.*, 1966, vol. 88, p. 4876.

29. Dillow, G.W. and Kebarle, P., *J. Am. Chem. Soc.*, 1989, vol. 111, p. 5592.

30. Egorochkin, A.N. and Voronkov, M.G., *Elektronnoe stroenie organicheskikh soedinenii kremniya, germaniya i olova* (Electronic Structure of Organic Silicon, Germanium, and Tin Compounds), Novosibirsk: Sib. Otd. Ross. Akad. Nauk, 2000.