

HALF-WAVE POTENTIALS OF QUINONE METHIDES IN DIMETHYLFORMAMIDE: SUBSTITUENT EFFECTS*

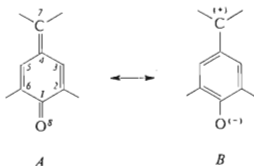
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Received January 24th, 1980

Half-wave potentials of two series of quinone methides *A* have been determined in 0.1M tetrabutylammonium perchlorate in dimethylformamide. The first series (type *I*; 14 compounds) contained fuchsones substituted in positions 2 and 2, 6 of the quinonoid ring, the second series (type *II* and *III*; 17 compounds) consisted of 2,6-ditert-butylquinone methides, with substituents at the exocyclic $C_{(7)}$ carbon atom. Properties of the first polarographic wave proved that in both series the reaction is a one-electron, reversible, diffusion-controlled process. Linear free energy relationship was found between $E_{1/2}$ and dual substituent constants σ_I and σ_R . Statistical analysis of linear free energy relationship for 2- and 2,6-substituted derivatives proved absence of steric factor in transmission of electronic substituent effect. The experimental results were interpreted on the basis of LUMO energies and spin densities, calculated by the HMO method.

Physico-chemical properties of quinone methides are in general determined by the relatively high electron densities in frontier orbitals¹ and by polarization, corresponding to the mesomeric structure *B*. According to carbonyl stretching vibrations^{2,3} and dipole moments^{4,5} of some derivatives, contribution of the dipolar structure *B* depends to a significant extent on substituents attached to the parent system. A greater contribution of the charge-separated form in compounds with strong electron donors attached to the $C_{(7)}$ carbon is indicated *e.g.* by the marked shift of the $\tilde{\nu}(C=O)$ and μ values on transition from 7,7-dicyano to 7,7-dipiperidino derivatives⁶ ($\Delta\tilde{\nu}(C=O) = 37 \text{ cm}^{-1}$, $\Delta\mu = 24.57 \cdot 10^{-30} \text{ C m}$). The effect of sub-

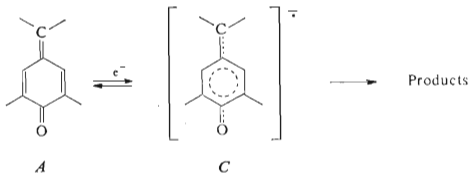


* Part XVII in the series Quinone Methides and Fuchsones; Part XVI: This Journal 45, 2675 (1980).

stituents in positions 2,6 is usually less significant; this can, however, be due to similar electronic properties of substituents in the studied compounds. An exceptional position have the bulky tert-butyl groups which in positions 2,6 stabilize the quinone methides more than would be expected from the purely electronic effect. Some authors^{4,7,8} do not exclude that the effect of these groups involves also steric factors.

For a quantitative evaluation of the overall substituent effects in positions 2,6 and 7, it is relatively difficult to find a measurable quantity which would sensitively enough reflect even differences between similar groups (*e.g.* alkyl groups). Determination of half-wave potentials represents one of the possible approaches, its advantage being moreover a relatively simple interpretation of experimental values by the LUMO orbital energy^{9,10}. Elucidation of relation between structure and half-wave potential for the cross-conjugated systems of quinone methides could extend also the existing knowledge on reduction of conjugated enones and serve as model also for similar systems, some of which are involved in biological processes¹¹. Concerning the relationship^{12,13} between n,π^* and π,π^* triplet energies and reduction potential, the electrochemical reduction of quinone methides might be of interest also in connection with sensibilization of photochemical processes.

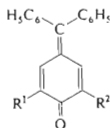
The electrochemical reduction of quinone methides has been hitherto studied only qualitatively on small series of compounds¹⁴⁻¹⁸, experiments in aqueous media¹⁴⁻¹⁶ being limited to fuchsone and its hydroxy derivatives (aurin). A two-electron mechanism was suggested¹⁴ for reduction of aurin at pH 7 in 30% ethanol; later, hydroxy derivatives of fuchsone were investigated in more detail^{15,16} over a broad range of pH. Electrochemical reduction of fuchsone and 7-substituted 2,6-ditert-butyl-7-cyanoquinone methides was studied in an aprotic medium^{17,18}. Crucial point of these investigations consisted in identification of structure of the intermediate, arising in the first reduction step (EPR spectrum) and in isolation of some products. It has been proved that in an aprotic medium the first reduction step is a reversible one-electron process leading to the anion-radical *C* (Scheme 1),



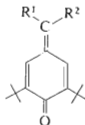
SCHEME 1

similarly as in the case of linearly conjugated enones^{19,20}. The hyperfine splitting constants prove that the delocalization degree of the unpaired electron depends on substituents attached to the C₍₇₎ carbon atom. Further reaction steps are not

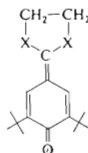
so unambiguous. According to the nature of the $C_{(7)}$ substituent (alkyl, cyano or piperidino group), the basic reaction (dianion formation) can be complicated by side processes, mainly dimerization and dismutation of the anion-radical¹⁸. The effect of substituents on polarographic behaviour of quinone methides in aprotic media have not been studied as yet.



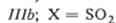
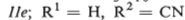
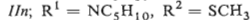
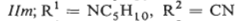
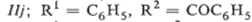
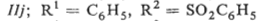
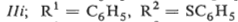
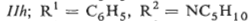
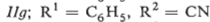
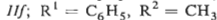
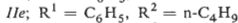
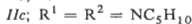
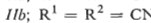
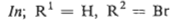
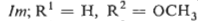
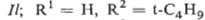
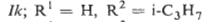
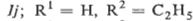
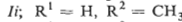
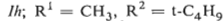
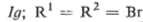
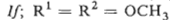
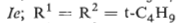
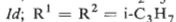
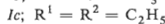
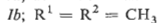
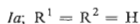
I



II



III



This paper concerns measurement of reduction potential of 31 quinone methides I–III in dimethylformamide on a dropping mercury electrode. The aim was to evaluate the effect of substituents in positions 2,6 (type I) and 7 (type II and III) on the first wave $E_{1/2}$ values and to interpret the experimental data on the basis of LUMO energies, spin densities and other HMO characteristics.

EXPERIMENTAL

Compounds

Quinone methides I–III were prepared by the known methods^{21–24} and their physical constants agreed well with the published values. Dimethylformamide was purified by repeated shaking with molecular sieves²⁵, followed by distillation *in vacuo*. The middle fraction (60% of the total amount) was used immediately after distillation. Tetrabutylammonium perchlorate (Fluka), used as electrolyte, was three times crystallized from methanol and dried in an exsiccator.

Polarographic Measurements

Apparatus: Polarographic curves were recorded on a digital polarograph²⁶, consisting of electronically generated voltage ramp, current-voltage convertor, digital voltmeter, convertor unit and tape punch. The instantaneous current was measured immediately before the end of control-

TABLE I
Half-Wave Potentials and Slopes for Polarographic Waves of Compounds I—III

Compound	$-E_{1/2}^I, \text{mV}^a$	Slope ^b	$-E_{1/2}^{II}, \text{mV}^a$	Slope ^b
<i>Ia</i>	445	59	897	48
<i>Ib</i>	582	62	964	45
<i>Ic</i>	597	64	994	59
<i>Id</i>	600	62	1 015	62
<i>Ie</i>	678	63	1 087	67
<i>If</i>	533	60	825	51
<i>Ig</i>	143	66	804	57
<i>Ih</i>	623	61	1 030	61
<i>Ii</i>	523	64	945	48
<i>Ij</i>	547	63	990	56
<i>Ik</i>	532	65	970	59
<i>Il</i>	538	64	982	59
<i>Im</i>	492	64	883	42
<i>In</i>	307	66	890	51
<i>IIa</i>	919	88	^c	
<i>IIb</i>	^d	—	536	^e
<i>IIc</i>	1 685	81	1 835	76
<i>IId</i>	629	70	1 335	95
<i>IIe</i>	840	58	1 322	77
<i>IIf</i>	787	63	1 330	73
<i>IIg</i>	196	65	757	62
<i>IIh</i>	1 076	65	^c	
<i>IIi</i>	596	73	^f	
<i>IIj</i>	238	79	1 324	66
<i>IIk</i>	360	59	976	80
<i>III</i>	1 315	50	^c	—
<i>IIIm</i>	509	63	1 104	94
<i>IIIn</i>	1 057	57	^c	—
<i>IIIo</i>	203	65	1 077	110
<i>IIIa</i>	891	48	^f	
<i>IIIb</i>	^d	—	^f	

^a Relative to saturated calomel electrode in the system LiCl/dimethylformamide; ^b in millivolts, referred to logarithmic unit; ^c no wave was observed in the studied potential region; ^d potential more positive than +200 mV (not measurable under the given experimental conditions); ^e not measured; ^f data not processed.

led drop life. During intervals between recording the current, the ramp voltage was recorded. The time interval between the current and voltage measurements and its relation to the end of the drop life was kept constant with two coupled electronic timers.

The measurements were performed in a Kalousek vessel, using the two-electrode arrangement. The dropping mercury electrode²⁷ had the controlled drop life $t_1 = 4.4$ s. At the polarization rate 100 mV/min the instantaneous current values were read at intervals of about 7.5 mV. The curves were recorded in the region of potentials ranging from that of dissolution of mercury (about +200 mV against the reference electrode) to about -1 600 mV, in both directions of the drop polarization. Potentials more negative than -1 600 mV were measured (at lower sensitivity) in the case of 4-bis(N-piperidyl)methylene-2,5-cyclohexadien-1-one (*IIC*) only. As the reference electrode a modified standard saturated calomel electrode which contained saturated solution of lithium chloride in anhydrous dimethylformamide proved to be advantageous. The lithium salt was used instead of sodium chloride usually employed in reference electrodes with dimethylformamide^{28,29} in order to avoid formation of the sparingly soluble sodium perchlorate at the phase boundary. Moreover, the viscous lithium chloride solution in dimethylformamide reduced the contamination of the electrode space. Reproducibility of the reference electrode potential was checked by measuring the half-wave potential of the positive wave of 2,6-ditert-butylfuchson at regular intervals.

An 0.1M solution of tetrabutylammonium perchlorate in dimethylformamide was used as the supporting electrolyte. Oxygen was removed by bubbling argon through the solutions. Concentration of all the studied depolarizers was $1 \cdot 10^{-3}$ mol \cdot l⁻¹; the observed currents were in the range 1—3 μ A.

Evaluation of polarographic curves: The data, recorded on a punched tape, were processed by a Hewlett Packard HP 9830A calculator. The half-wave potentials $E_{1/2}$ and the reciprocal logarithmic slopes of the polarographic waves λ were obtained by approximation (least squares) of the dependence of the instantaneous current i on the applied polarization potential E with the relation:

$$\lambda \log [(i_{lim} - i)/i] = E - E_{1/2},$$

where i_{lim} denotes the limiting wave current and $\lambda = \alpha n \cdot F/2 \cdot 3RT$ (with the usual symbols for transfer coefficient, number of electrons, Faraday charge, gas constant and absolute temperature). For some compounds the curve shape was tested³⁰ for an interposed fast dimerization reaction, following the first one-electron reduction step.

The half-wave potentials in Table I are mean values obtained from both directions of drop polarization. Repeated checks of the reference electrode gave the standard deviation of about ± 3 mV which corresponds to 90% confidence limits of about ± 6 mV.

Calculations

Statistical treatment: Quantitative relationships between the experimentally measured half-wave reduction potentials and substitution constants or quantum-chemical characteristics were evaluated on a HP 9830A calculator using the standard program for a multiple linear regression (Hewlett Packard Standard Statistic Pac No 2). The correlation dependences were tested using the multiple coefficient, partial and total F-test and Student t-test.

Quantum-chemical calculations: The π -electron structure of all the 31 compounds was investigated by the simplest HMO procedure. The calculations were performed on an IBM 370/135 computer using the standard program and recommended parameter set^{31,32}. The given parameter

set was extended by addition of parameters describing the zwitterionic structure *B*. For sulfur-containing compounds the values $h(\text{S}^{\delta+}) = 2.0$ and $k(\text{C}-\text{S}^{\delta+}) = 0.53$ were used. According to previous experience³³, the Coulombic integral for the quaternary nitrogen in the amine-containing compounds was taken as 2.5 instead of 2.0. Investigation of electronic absorption spectra of quinone methides with two more bulky groups in position 7 has shown that these substituents deviate from the quinone methide plane. The deviation angle, determined by comparison of the shift of the longest-wave absorption band in these compounds relative to its position in spectra of unsubstituted and monosubstituted compounds³⁴, was incorporated into the corresponding resonance integral using the relationship $\beta_{\gamma} = \beta_0 \cdot \cos \gamma$.

RESULTS AND DISCUSSION

Under given experimental conditions, compounds *I-III* afforded well developed polarographic curves. Almost in all cases the curves exhibited two separated waves of approximately the same height whose slopes (λ) and corresponding half-wave potentials ($E_{1/2}$) are given in Table I; a typical course of reduction for compounds *Ie* and *IIIk* is depicted in Fig. 1. The λ values for the first polarographic wave of almost all compounds are close to the value corresponding to one-electron reversible reduction according to Scheme 1. In derivatives *IIb* and *IIIb* the strong electron-acceptor effect of the cyano or sulfonyl groups makes the electron transfer so easy that the wave due to the first reduction step begins directly at the potential of dissolution of mercury. Therefore, it was not possible to determine the $E_{1/2}$ values for these compounds with the given experimental arrangement.

The effect of substituents on the half-wave potential of the first reduction step of compounds *I-III* was assessed quantitatively using the two-parameter equation (1).

$$E_{1/2} = \varrho_1 \sum \sigma_I + \varrho_R \sum \sigma_R + C \quad (1)$$

Statistical treatment of this equation for the whole set of compounds (Table II) indicates that the effect of 2,6- and 7-substituents on reduction of quinone methides is additive, the contribution of the inductive mechanism to the total transmission being about 60%. Although the statistical parameters are satisfactory ($r = 0.968$; $F_{101} = 192$), it must be taken into account that the range of potential values for compounds *I* is 500 mV whereas for compounds *II* and *III* it amounts to 1900 mV. The overall correlation is thus controlled by compounds of the type *II* and *III* and the conclusion, drawn from this correlation, *i.e.* that transmission of the effect from positions 2,6- and 7- is identical, may not be correct. A more detailed analysis of this problem requires the statistical treatment of equation (1) to be performed separately for both the series of compounds. As seen from Fig. 2, such separate treatment results in splitting of the overall correlation into two partial ones, according to the substituent position. The statistical parameters of equation (1) further show that the ratio

of inductive to resonance mechanism is approximately the same (3:2) but the transmission is greater for compounds *II* and *III* than for compounds *I*. This holds for the inductive ($q_I^{II,III}/q_I^I = 1.646$) as well as for the resonance ($q_R^{II,III}/q_R^I = 1.794$) component of the electronic effect. These results support the assumption that the reaction center is at the $C_{(7)}$ carbon atom since the inductive effect which for both series represents a major component of the overall effect depends in general on the distance. The effect of substituents in positions 2,6 must be thus weaker than that of substituents on $C_{(7)}$ carbon atom. A higher sensitivity of $E_{1/2}$ towards substitution at $C_{(7)}$ is indicated also by HMO calculations of squares of expansion coefficients (Table III) which witness predominant localization of the LUMO orbital at the $C_{(7)}$ center. We checked also the possible participation of a steric effect in substituent effect transmission. According to the HMO calculations, the highest electron affinity exists at the $C_{(1)}$ and $C_{(7)}$ atoms ($a_{(1)} > Q_{(7)}$ for fuchsones and quinone methides with electron-accepting groups at $C_{(7)}$; $Q_{(1)} < Q_{(7)}$ for other quinone methides). In order to describe the steric factor contribution in the vicinity of these two centers, i.e. both for the substituents in position 2,6 and in position 7, we applied the three-parameter equation (2) to both series of quinone methides.

$$E_{1/2} = q_I \sum \sigma_I + q_R \sum \sigma_R + \delta \sum R_M + C \quad (2)$$

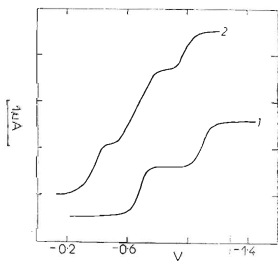


FIG. 1

Polarographic Curves of Quinone Methides *Ie* (curve 1) and *IIk* (curve 2) after Smoothing and Correction for Capacity Current

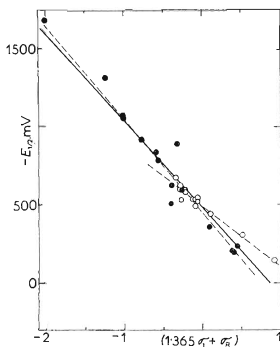


FIG. 2

Dependence of $E_{1/2}$ of Compounds *I—III* on Substituent Constants q_I and q_R

Dashed lines denote splitting of the correlated data into two classes; fuchsones *I* (○), quinone methides *II* and *III* (●).

Statistical analysis of thus-obtained results showed in both cases insignificance of the third term ($F_{\text{part.}} = 0.03 - 0.54$, $t_{\text{part.}} = 0.17 - 0.74$) which involves (as molar refractions R_M) steric demands of substituents. It is therefore obvious that steric effects affect the transmission neither from the positions 2,6 nor from the position 7.

The dependence of $E_{1/2}$ on energy of the LUMO orbital for quinone methides *I–III* is given in Fig. 3. Even without calculation it is evident that there does exist a correlation between both these quantities but that its goodness is worsened by data

TABLE II
Statistical Treatment of Equation (1)

Series	Q_1^a	t_1^b	Q_R^a	t_R^b	C	r^c	s_{est}^d	F^e
<i>I</i>	529.16 (21.7)	24.4	323.59 (22.2)	14.6	-473.21 (7.6)	0.9909	20.09	298.9
<i>I^f</i>	561.45 (20.5)	27.4	432.23 (25.3)	17.1	-447.13 (7.2)	0.9949	15.87	321.8
<i>II, III</i>	870.83 (86.0)	10.1	580.43 (41.0)	14.2	-739.68 (40.8)	0.9806	87.28	162.5
<i>I–III</i>	748.50 (56.8)	13.2	548.41 (34.8)	15.8	-479.16 (28.8)	0.9677	88.98	191.8

^a Coefficients of equation (1) with standard deviations in parentheses; ^b values of the Student *t*-test; ^c multiple correlation coefficient; ^d standard deviation; ^e values of the total Fisher–Snedecor *F*-test; ^f statistical parameters of equation (2) ($\delta = -0.36 \pm 0.5$; $t_\delta = 0.7$).

TABLE III
Some of HMO Reactivity Indices of Compounds *Ia*, *Iib* and *Iic*

Compound	$S_n(1)^a$	$S_n(7)^a$	$S_e(8)^a$	I_R^{Tb}	I_R^{LUMOc}	$\epsilon^{\text{HOMO}}(\beta)$	$\epsilon^{\text{LUMO}}(\beta)$
<i>Ia</i>	2.50	4.17	1.53	0.89	2.15	0.6005	-0.1300
<i>Iib</i>	7.59	12.72	1.37	0.61	1.80	0.6998	-0.0379
<i>Iic</i>	1.47	3.64	1.00	3.72	3.62	0.9774	-0.2971

^a Numbers 1, 8 refer to the carbonyl carbon and oxygen atoms, respectively, number 7 denotes the exo-carbon atom $C_{(7)}$; ^b $I_R^{\text{T}} = Q(7)/Q(1)$; ^c $I_R^{\text{LUMO}} = (c^{-1})_7^2 / (c^{-1})_1^2$.

for six compounds (*Iic*, *Iih*, *Iil*, *Iim*, *Iin* and *IIIa*) whose LUMO energies are substantially lower than expected. All these compounds contain a strong electron donor at $C_{(7)}$ and exhibit high dipole moment⁶ ($20-40 \cdot 10^{-30}$ C m). We can therefore assume that the overall electron distribution in their molecules corresponds to the zwitter-ionic structure *B* rather than to the quinonoid structure *A*. The observed discrepancies can thus be ascribed to the chosen parameterization which does not describe the structure with a sufficient accuracy. After HMO reparameterization for these six compounds according to the model *B*, the final correlation (3) is obtained:

$$E_{1/2} = (7678.0 \pm 240.6) \varepsilon^{\text{LUMO}} + (543.6 \pm 36.8), \quad (3)$$

($r = 0.988$, $s = 44.8$ and $F_{\text{tot}} = 1017.2$ ($n = 28$)). The only one compound, whose parameters do not fit significantly after the reparameterization, is the dipiperidino derivative *Iic* ($E_{1/2}^{\text{calc.}} - E_{1/2}^{\text{found}} = 410$ mV). In this case the slope ($\lambda = 81$) exceeds by 21 units the theoretical value for a one-electron reversible process (Table I). Thus,

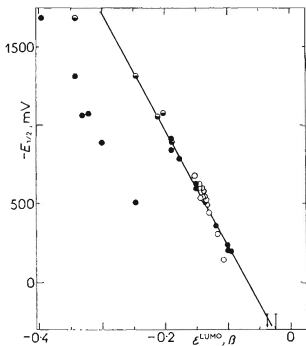


FIG. 3

Dependence of $E_{1/2}$ of Compounds *I-III* on Their LUMO Orbital Energy

For description of the points see Fig. 2; \bullet parameterization according to HMO model of the type *B*.

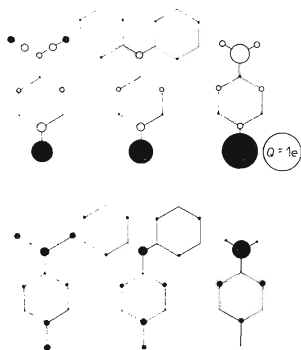


FIG. 4

Molecular Diagrams of Charge Distribution and Spin Densities for *p*-Fuchsone (*Ia*), 4-Dicyanomethylene-2,5-cyclohexadien-1-one (*Iib*) and 4-Bis-*N*-piperidylmethylene-2,5-cyclohexadien-1-one (*Iic*).

in a first approximation, we might assume that one of the fundamental requirements of the correlation, namely the reversibility of the process, is not fulfilled. However, the fact that the dimethyl derivative *Ila* with about the same slope ($\lambda = 88$) fits the correlation, speaks against this assumption. A deviation from reversibility is thus obviously not significant enough to lead alone to a correlation failure. Since the compound *Ilc* is the only derivative of the studied series which exhibits a negative solvatochromism⁶, we can expect that also changes due to solvation in the polarographic reduction of this compound will differ from those for other compounds. Thus, a probable reason of the deviation of compound *Ilc* from the correlation (3) is that another of the general requirements of the relationship $E_{1/2} = f(e^{L_{UMO}})$ is not satisfied: the requirement of insignificance of solvation-induced changes or at least their linear dependence on the correlated quantity in the whole studied series of compounds.

Molecular diagrams of charge distribution and spin densities in three typical representants of the studied compounds *Ia*, *Iib* and *Iic*, reflect distinctly the extent of perturbation of the fundamental electronic structure of the molecule caused by various substituents on the $C_{(7)}$ carbon atom (Fig. 4). Whereas the strongly electron-accepting cyano groups in 7,7-dicyano-2,5-cyclohexadien-1-one (*Iib*) hinder substantially skeletal polarization ($Q_{C(1)} + 0.24 e$, $Q_{C(7)} + 0.10 e$ and $Q_{O(8)} - 0.58 e$) in the 7,7-dipiperidino derivative *Iic*, the polarization of the π -electronic system is significant ($Q_{C(1)} + 0.14 e$, $Q_{C(7)} + 0.52 e$ and $Q_{O(8)} - 0.92 e$). Fuchson *Ia* lies between these two extremes, its charge distribution ($Q_{C(1)} + 0.21 e$, $Q_{C(7)} + 0.18 e$ and $Q_{O(8)} - 0.65 e$) corresponding to a weak electron-acceptor character of the phenyl groups bonded to the exocyclic carbon atom.

Contrary to majority of quinone methides *I-III*, in compounds with strongly electron donating substituents in position 7, the unpaired electron is localized to an extent of 44–52% at the $C_{(7)}$ atom. This high localization predicts a dimerization tendency of these compounds (if other, *e.g.* steric, conditions are favourable). Compounds *III* ($(c^{-1})_7^2 = -0.506$) and *IIIa* ($(c^{-1})_7^2 = -0.516$) may serve as an example. The dimerization tendency in them is confirmed also by the experimentally found low slope values (50 mV and 48 mV). Diagnostic tests have also shown that for these compounds the shape of the positive reduction wave corresponds to an approximate relationship³⁵ for a rapid dimerization following the electronic process rather than to an equation for a reversible polarographic wave. The dimerization in reaction of *IIIa* was moreover confirmed³⁶ also by the shape of the negative wave.

Polarographic curves of quinone methides, substituted (besides phenyl) with reducible groups (*e.g.* COC_6H_5) at $C_{(7)}$, exhibit in addition to the usual waves a steep, twice as high, wave appearing between both one-electron steps (Fig. 1). We assume that this wave corresponds to reduction of the groups or to a reductive fragmentation of the molecule. This assumption is supported also by the quantum chemical reactivity indices found for the parent structure *Iij* ($S_n(7) = 3.96$, $S_n(1) =$

= 3.27, $S_n(\text{COC}_6\text{H}_5) = 2.85$) and for the formed anion-radical ($S_n(\text{COC}_6\text{H}_5) = 2.30$, $S_n(7) = 2.25$, $S_n(1) = 1.96$). No more detailed study of these two-electron waves has been carried out.

The following conclusions can be drawn from the present study: 1) Positive inductive and resonance substituent effects suppress the electron affinity of quinone methides and shift the half-wave potential to more negative values; 2) the reduction potential in the series I–III is affected more by substituents at $C_{(7)}$ than at $C_{(2)}$ and can be interpreted on the basis of the LUMO orbital energy; 3) the inductive mechanism represents a major contribution (about 60%) to the electronic substituent effect transmission; 4) there is no contribution of steric effect; 5) the dimerization tendency of anion-radicals derived from quinone methides with strong electron donors at $C_{(7)}$ is caused by prevailing localization of the unpaired electron at the $C_{(7)}$ center.

Thanks are due to Dr A. Vitek, Institute of Organic Chemistry and Biochemistry, for computer programs and discussion to the numerical treatment of the experimental data.

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Translated by M. Tichý.