more bulky in the dimer of radical (V) than in (I)-(IV). This gives rise to still more marked hindrances to twisting vibrations in the transition state for decomposition of dimer (V). An increase in the transition state rigidity leads to a reduction in the A_{-1} value.

CONCLUSIONS

1. Kinetic and thermodynamic parameters have been determined for the $2\Phi^{\bullet} \rightleftharpoons \Phi-\Phi$ system, $\Phi^{\bullet}$ being a 2-(4'-dialkylaminophenyl)-1,3-indandionyl radical.

2. Recombination of $\Phi^{\bullet}$ radicals is a diffusion-limited process.

3. The $\Phi-\Phi$ dimers are thermochromic and photochromic compounds.

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THE ELECTROCHEMICAL REDUCTION OF METHYLENEQUINONES

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UDC 541.138.3:547.567

Although it has long been known that the electrochemical reduction of quinones and certain quinolide compounds proceeds through reversible radical-anion formation [1, 2], there has been little study of the analogous methylenequinone reactions.

The present work was a study of the polarographic reduction of 15 stable 2,6-di-tert-butylmethylenequinones with various substituents in the methylene unit. The polarograms were developed in DMFA solution (dropping mercury electrode), using 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte. Anodic waves were recorded with the aid of a Kalousek switch operated at frequencies ranging from 2 to 50 Hz. Some of the anodic–cathodic waves were reversible, and some partially reversible or irreversible, depending on the type of substituent in the methylenequinone molecule.

It is clear that there are many points of similarity between the polarographic reduction of the methylenequinones and the quinones. In general, the initial step in polarographic reduction of methylenequinones leads to the formation of a radical anion which dimerizes, or is reduced to the dianion. Polarographic reduction of

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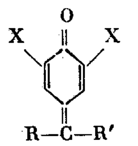
TABLE 1. Half-Wave Potentials (sat. cal. elec.) and Saturation Currents for the Polarographic Reduction of Various Methylenequinones ($4.7 \cdot 10^{-4}$ mole/liter DMFA, 0.1 M tetrabutylammonium perchlorate supporting electrolyte, 25°)



Compound	R	R'	$-E_{1/2}$, V	i_d, μA	$-E_{1/2}$, V	i_d, μA
(I)	C_6H_5	C_6H_5	1,12	1,5	1,61	1,3
(II)	CN	CN	0,12	1,5	0,99	1,2
(III)	C_6H_5	CN	0,57	1,4	1,13	0,9
(IV)	CH_3	CN	0,75	1,7	1,48	0,2
(V)	C_2H_5	CN	0,77	1,6	1,49	0,2
(VI)	$CH(CH_3)_2$	CN	0,78	1,8	1,50	0,3
(VII)	H	H	1,18	1,6	1,46	0,3
(VIII)	H	CH_3	1,31	1,2	2,10	0,4
(IX)	H	$CH(CH_3)_2$	1,37	1,5	–	–
(X)	H	C_6H_5	1,07	1,6	–	–
(XI)	H	CN	0,64	1,5	–	–
(XII)	H	OCH_3	1,50	1,1	–	–
(XIII)	H	NC_5H_{10}	1,78	0,9	1,99	0,2
(XIV)	H	Cl	1,01	2,8	–	–
(XV)	CH_3	CH_3	1,37	1,4	–	–

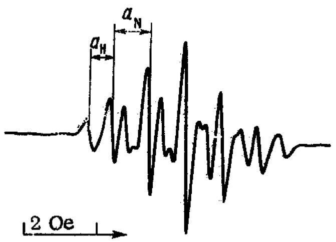
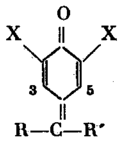


Fig. 1. ESR spectrum of the radical anion formed in the electrochemical reduction of α,α-dicyano-2,6-di-tert-butylmethylenequinone.

TABLE 2. Parameters for the ESR Spectra of the Radical Anions Formed in the Reduction of Methylenequinones



(hyperfine splitting constants, Oe)

R and R'	a_H^3	a_H^5	a_R	a_R
R=R′=CN	0,65 0,5	0,65 0,5	1,05 1,05	1,05 1,05
R=CN R′=C_6H_5	0,8	0,8	$a_N^{CN}=1,7$	$a_H^o=1,7$ $a_H^p=5,1$
R=CN R′=$CH(CH_3)_2$	2,7	2,7	$a_N^{CN}=2,0$	$a_H^{CH}=4,7$ $a_H^{CH_3}=0,3$
R=R′=C_6H_5	2,25	2,25	$a_H^o=2,25$ $a_H^p=2,6$ $a_H^m=1,0$	$a_H^o=2,25$ $a_H^p=2,6$ $a_H^m=1,0$

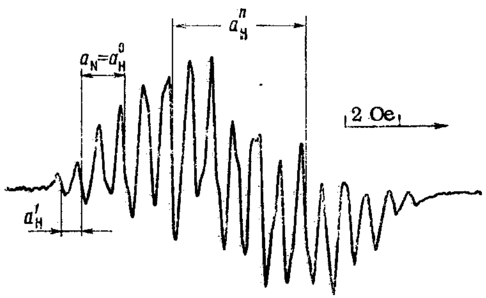
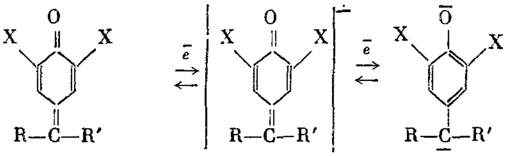


Fig. 2. ESR spectrum of the anion radical obtained in the electrochemical reduction of α-phenyl-α-cyano-2,6-di-tert-butylmethylenequinone.

the methylenequinones (I)-(III), each with two electronegative substituents, gives rise to two reversible, one-electron diffusion waves (Table 1), one for the formation of the radical anions (Ia)-(IIIa), and the other for subsequent reduction to the dianion form. The radical anions (Ia)-(IIIa) can be obtained from (I)-(III), either by electrochemical reduction or by interaction with metallic potassium (THF).



$X = C(CH_3)_3$; $R = R' = C_6H_5$ (I); $R = R' = CN$ (II), $R = CN$, $R' = C_6H_5$ (III)

(Ia)—(IIIa)

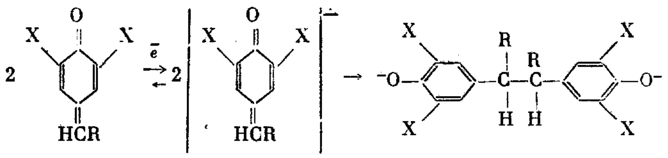
The spectrum of radical anion (Ia) has been described in [3]. Because of hyperfine interaction of the unpaired electron with the two equivalent nitrogen nuclei, the spectrum of (IIa) (Fig. 1) has the form of a quintuplet (1.05 Oe), each component of which is split into a triplet (0.65-0.5 Oe) on the ring protons. The α-phenyl-α-cyano-2,6-di-tert-butylmethylenequinone (III) yields the radical anion (IIIa), the latter showing a well-resolved ESR spectrum with the hyperfine splitting constants listed in Table 2 (Fig. 2). The polarographic half-wave potentials for reduction of the individual radical anions (Ia)-(IIIa) proved to be identical with the half-wave potentials for reduction of the respective (I)-(III) methylenequinones. As a result, electrolysis of (I)-(III) at second-wave potentials leads to the formation of the 4-substituted 2,6-di-tert-butylphenols (after treatment with acid), the coulometric data indicating that it is here a matter of a two-electron reduction process.

Although the first-wave slopes were such as to indicate that the polarographic reduction of the α-alkyl-α-cyano-2,6-di-tert-butylmethylenequinones proceeds irreversibly ($\alpha n = 0.5-0.7$), polarograms obtained with the Kalousek switch (f = 12.5 Hz) showed the flat anodic–cathodic waves characteristic of reversible processes. The second-wave saturation current for polarographic reduction of these compounds is 10-15% of the first-wave saturation current, the waves themselves clearly arising from dianion formation. Well-resolved ESR spectra could not be obtained in the electrochemical reduction of the methylenequinones (IV)-(VI), and this despite the fact that a good spectrum of the radical anion (VIa) was obtained through reduction of α-isopropyl-α-cyano-2,6-di-tert-butylmethylenequinone (VI) by metallic K in THF solution (cf. Table 2).

Interpretation of the results obtained in the electrolysis of methylenequinones with substituents carrying α-H atoms is made complicated by the fact that electrolysis is here accomplished by isomerization to derivatives of 4-vinyl-2,6-di-tert-butylphenol. For example, electrolysis of the methylenequinone (VI) (n = 0.84, according to the coulometric data) gave a mixture of 4-(α-isopropyl-α-cyano)methyl-2,6-di-tert-butylphenol and 1-cyano-(4-hydroxy-3,5-di-tert-butylphenyl)-2,2-dimethylethylene. The catalytic isomerization of the methylenequinones to vinylphenols has already been reported [4]. The data obtained in the electrolysis and polarographic reduction of (VI) suggest that reaction of the radical anions (IVa)-(VIa) is principally through disproportionation.

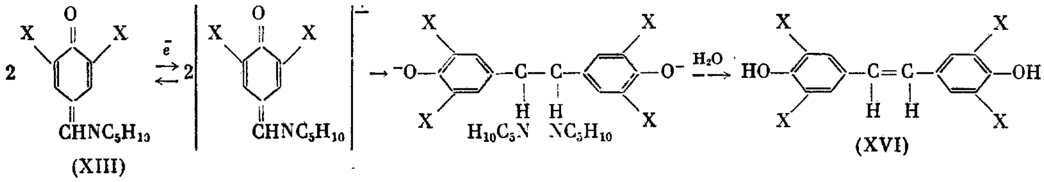
The radical anions of the (VII)-(XV) methylenequinones are unstable and readily disproportionate. Electrolysis of (VII)-(XV) leads to the formation of various dimers with logarithmic concentration vs half-wave potential relations of the type previously described in [5]. Increasing the concentration of these compounds reduces the curvature of the wave and eventually leads to its separation into two other waves, an effect frequently met at high dimerization constants of the radicals. In certain cases, polarographic reduction of these compounds led to the appearance of low saturation current waves which disappeared when the concentration was carried above 10^{-3} mole/liter. Polarograms for these compounds obtained with the Kalousek switch showed partially reversible, or irreversible, waves, and ordinary reduction waves with transfer coefficients in the neighborhood of unity at depolarizer concentrations less than $5 \cdot 10^{-4}$ mole/liter, thus suggesting that direct electrochemical reaction (pseudoreversible wave) proceeds rapidly in these systems. Exceptions here were α-isopropyl-2,6-di-tert-butylmethylenequinone and the α,α-dimethyl analog for which $\alpha = 0.3-0.4$.

Electrolysis of the methylenequinones (VII)-(XII) led to the formation of derivatives of 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenylethane as products from the dimerization of various radical anions.

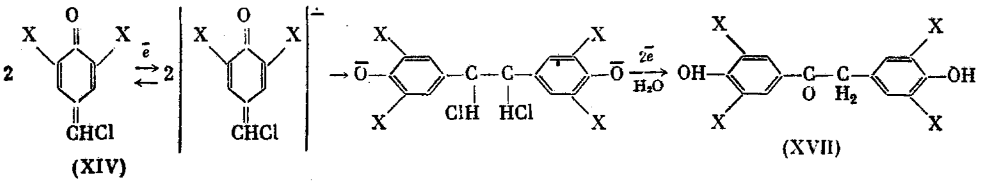


R=H (VII), CH_3 (VIII), $CH(CH_3)_2$ (IX), C_6H_5 (X), CN (XI), OCH_3 (XII).

The fact that electrolysis of α-piperidyl-2,6-di-tert-butylmethylenequinone (XIII) led to the formation of 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxyphenylethylene (XVI) suggests that electrochemical reduction proceeds here through substituent elimination. Since the overall reduction of the methylenequinone (XIII) is a one-electron process ($n\alpha = 1.14$), the dihydroxydiphenylethylene (XVI) must obviously be formed in the reaction



Two-electron electrochemical reduction of α-chloro-2,6-di-tert-butylmethylenequinone (XVI) followed by a series of successive reactions gave a 68% yield of α-(4-hydroxy-3,5-di-tert-butylphenyl)-4-hydroxy-3,5-di-tert-butylacetophenone (XVII)



The data of polarographic, coulombic, and ESR studies suggest that the primary act in the electrochemical reduction of methylenequinones is the formation of a radical anion whose properties are determined by the nature of the substituent at the C atom of the methylene grouping. The nature of this substituent also has a marked effect on the energy of the lower free molecular orbital of the methylenequinone, thereby affecting the reactivity in one-electron transfer processes.

EXPERIMENTAL

The methylenequinones were prepared by oxidizing the respective phenols in benzene solution, following the methods of [6, 7]; the constants of the methylenequinones described earlier agreed with the values reported in [8]. Similar methods were followed in synthesizing α-ethyl-α-cyano-2,6-di-tert-butylmethylenequinone (V): mp 46-48°C; λ_{max} 310 nm; log ε 4.58; λ_{max} 323 nm, log ε 4.60. Found: C 79.61; H 9.20%. $C_{17}H_{25}ON$. Calculated: C 79.66; H 9.29%. For compound (VI): mp 106-107°C; λ_{max} 310 nm, log ε 4.60; λ_{max} 323 nm, log ε 4.61. Found: C 79.88; H 9.40%. $C_{18}H_{27}ON$. Calculated: C 79.95; H 9.54%. For compound (III): mp 109-110°C, λ_{max} 355 nm, log ε 4.50. Found: C 82.60; H 7.82. $C_{21}H_{25}ON$. Calculated: C 82.72; H 7.89%. The methylenequinone (II) was synthesized by the procedure of [9]: mp 127-128°C; λ_{max} 335 nm, log ε 4.51.

Polarographic measurements were carried out with a dropping mercury electrode LP-7 polarograph. The capillary constants were: $m = 1.64$ mg/sec; $t = 3.2$; $h = 73$ cm. Comparison was against a detachable saturated calomel electrode, without phase potential correction; the cell resistance was 3000 Ω. Electrical measurements were made with a P-5848 potentiostat equipped with a current integrator. The procedures followed in electrolysis have been described in [10]. The mass left at the end of electrolysis was neutralized with 1 N HCl, the resulting solution diluted with water, and the whole extracted with ether. Crystallization gave the following products: from (I), 4-(α,α-diphenyl)methyl-2,6-di-tert-butylphenol, 92% yield, mp 133-134°C (according to [11], mp 134°C); from (II), 4-(α,α-dicyano)methyl-2,6-di-tert-butylphenol, 88% yield, mp 156-158°C. Found: C 75.32; H 8.22%. $C_{17}H_{22}ON_2$. Calculated: C 75.52; H 8.20%. From (III) there was obtained 4-(α-phenyl-α-cyano)methyl-2,6-di-tert-butylphenol, 98% yield, mp 104-105°C (heptane) (according to [12], mp 104°C); from (VI), 4-(α-isopropyl-α-cyano)methyl-2,6-di-tert-butylphenol, 32% yield, mp 85-87°C (heptane) (according to [12], mp 85-87°C) and 1-cyano-1'-(4-hydroxy-3,5-di-tert-butylphenyl)-2,2'-dimethylethylene, 56% yield, mp 110-111°C (hexane). Found: C 79.77; H 9.52%. $C_{18}H_{27}ON$. Calculated: C 79.95; H 9.54%. PMR spectra (CCl_4, δ, ppm): 1.1 s $[C(CH_3]_3$, 1.42 s (CH_3), 1.62 s (CH_3), 4.8 s (OH), 7.15 s (CH). IR spectra (ν, cm^{-1}): 3640 (OH). From (VII) there was obtained 3,3'5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenylethane, 98% yield, mp 173-174°C (according to [13], mp 172°C); from (VIII), 1,2-dimethyl-(3,3'5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenyl)ethane, mp 157-158°C (hexane), 64% yield. Found: C 82.16; H 10.71%. $C_{32}H_{50}O_2$. Calculated: C 82.35; H 10.80%. From (IX) there was obtained 1,2-diisopropyl-(3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenyl)ethane, 58% yield, mp 298°C (sublimes). Found: C 82.55; H 11.19%. $C_{36}H_{58}O_2$. Calculated: C 82.70; H 11.18%. From (X) there was obtained 1,2-diphenyl-(3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenyl)ethane 97% yield, mp 205-206°C (sublimes). Found: C 85.49; H 9.24%. $C_{42}H_{54}O_2$. Calculated: C 85.37; H 9.21%. From (XI) there was obtained 1,2-dicyano-(3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenyl)ethane, 88% yield, mp 208-210°C (heptane–benzene). Found: C 78.58; H 9.02%. $C_{30}H_{44}O_2N_2$. Calculated: C 78.65; H 9.07%. From (XII) there was obtained 1,2-dimethoxy-(3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenyl)ethane, 78% yield, mp 120-121°C. Found: C 77.12; H 9.98%. $C_{32}H_{50}O_4$. Calculated: C 77.06; H 10.11%. IR spectra (ν, cm^{-1}): 1150 (OCH_3). From (XIII) there was obtained 3,3',5,5'-tetra-tert-butyl-4,4'-dihydroxydiphenylethylene, 85% yield, mp 242-244°C (according to [13], mp 244°C); from (XIV) α-(4-hydroxy-3,5-di-tert-butylphenyl)-4-hydroxy-3,5-di-tert-butylacetophenone, 68% yield, mp 240-241°C (heptane). Found: C 79.12; H 9.66%. $C_{30}H_{44}O_3$. Calculated: C 79.61; H 9.70%. IR spectrum (ν, cm^{-1}): 1682 (C=O). Structures for the various compounds were confirmed by IR and PMR spectroscopy.

CONCLUSIONS

1. The details of the electrochemical reduction of the methylenequinones are determined by the properties of the radical anions that appear in the system as reaction intermediates; these can undergo further reduction, dimerize, or disproportionate.

2. Analysis of the ESR spectra of four different compounds confirmed the formation of radical anions in the course of these reduction reactions.

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