# ESR SPECTRA OF ELECTROCHEMICALLY GENERATED
FREE ANION RADICALS OF HETARYL-SUBSTITUTED
TRICHLORO-1,4-BENZOQUINONES

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The ESR method was used to confirm the formation of free anion radicals in the source of electrochemical reduction of 5-thiazolyl-substituted 1,4-benzoquinones and related compounds, as well as the ability of the unpaired electron to become delocalized over the system of π electrons not only of the benzoquinone nucleus but also of the hetaryl substituent added to it.

In order to determine the electronic interactions between electron-donor heterocycles and the electron-acceptor 1,4-benzoquinone fragments, we synthesized hetaryl-substituted trichloro-1,4-benzoquinones. Several methods of preparation of such compounds are known [1], but a general method of synthesis of hetaryl-substituted 1,4-benzoquinones has been proposed only recently [2]. The present paper deals with the ESR spectra of the electrochemically generated anion radicals of these compounds.
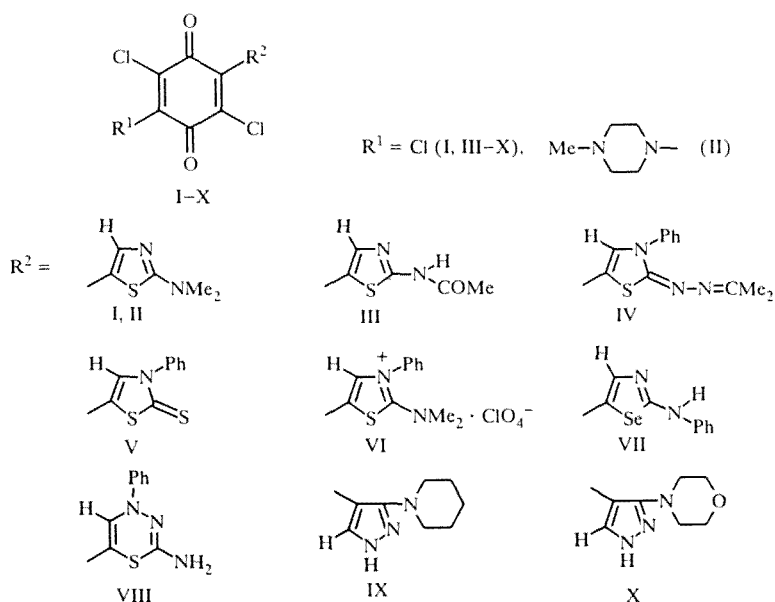
On the basis of the preliminary results of studies[*] of the electrochemical reduction of compounds I-X, which indicate the one-electron nature of the first step of their reduction at a mercury microelectrode ($E_{1/2}$, from +0.05 to −0.55 V relative to an aqueous saturated calomel electrode), it was postulated that primary free anion radicals of semiquinone structure are formed in this process. To confirm this hypothesis and determine the structural characteristics of the indicated particles, we attempted in this work to record their ESR spectra.

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*The results of the electrochemical study will be published separately.

TABLE 1. Values of Electrochemical Generation Potentials (E_{rel}, Pt el.), Values of g Factor, HFS Constants (a_H, G) and Linewidths (ΔH, G) of ESR Spectra of Free Anion Radicals of Compounds I-X

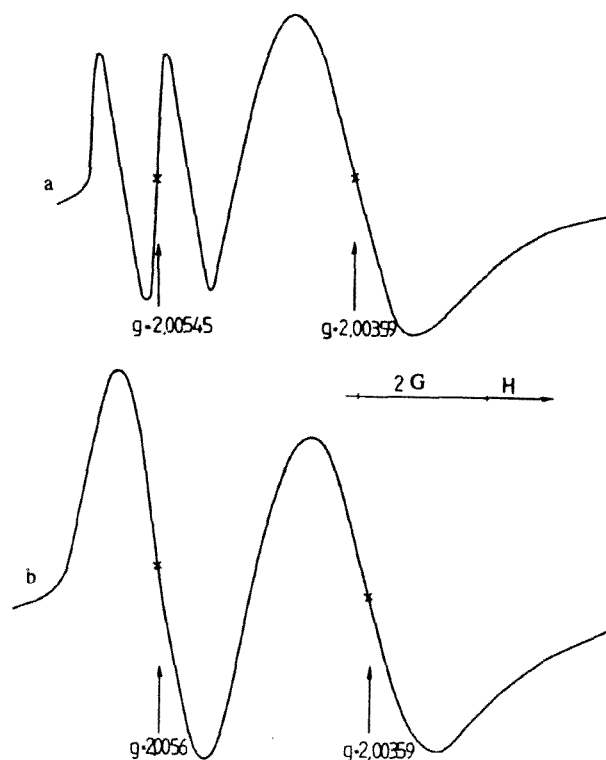| Compound	$-E$	g	a_H	ΔH
I	0,5	2,00570	0,98	~0,7
II	0,4	2,00513	~1,2	~1,0
III	0,4	2,00554	0,71	0,15
IV	0,5	2,00545	0,94	~0,5
V	0,5	2,00551	1,02	0,36
VI	0,4	2,00554	1,21	~0,5
VII	0,3	2,00535	1,16	~0,5
VIII	0,4	2,00560	—	~1,1
IX	0,5	2,00570	—	~0,3
X	0,4	2,00571	—	~0,3

Fig. 1. ESR spectra of anion radicals of compounds IV (a) and VIII (b) in acetonitrile (for comparison — simultaneously recorded signal of polycrystalline 1,1-diphenyl-2-picrylhydrazyl, g = 2.00359).

Our method of electrochemical generation (ECG) [3] was used to obtain the ESR spectra of free radicals — unstable intermediate particles in the electrochemical reduction of compounds I-X acetonitrile. The ESR spectra of these radicals either consist of a single signal (compounds VIII-X̣), or they have a doublet hyperfine structure (HFS) caused by a single proton (compounds I-VII) (Fig. 1). Values of the parameters characterizing the ESR spectra of the free radicals obtained are listed in Table 1. The values of the g factor of these radicals are intermediate between the values corresponding to the anion radicals of 1,4-benzoquinone and of tetrachloro-1,4-benzoquinone [4].

The HFS values of the ESR spectra indicate that the unpaired electron in the corresponding free radicals not only is delocalized over the system of π electrons of 1,4-benzoquinone, this being characteristic of this class of compounds, but can also interact with the proton of the thiazole (I-VI) or selenazole (VII) substituent. However, the interaction of the unpaired electron with the nucleus of the nitrogen atom, which is also present in the conjugated system of π electrons of these

substituents, is not clearly observed. This may be due to the low value of the HFS constant, determined by this nucleus. As has been demonstrated (for example, in the case of a vinyl substituent), the values of the HFS constants depend on the location of the nuclei in such a conjugated system and are arranged as follows: $C\beta > C\alpha > C\gamma$ [5]. This assumption can be confirmed by the increased width (ΔH) of the HFS signals, this being observed for all the ESR spectra of the indicated compounds except compound III. This broadening is apparently a consequence of unresolved HFS caused by the interaction of the unpaired electron with other nuclei of the atoms of the hetaryl group of the free radical. The absence of such broadening for the free radical of compound III may indicate the possibility of interaction of the unpaired electron with the proton of the substituent via the superconjugation mechanism as well. The latter conclusion may also be reached by comparing the spectra of the free radicals of compounds VIII and V, in which the CH fragment of the heterocycle is located in approximately the same environment, but the HFS of these spectra is different.

The value of the HFS constant a_H of the ESR spectra of the compounds studied, which is determined by the proton of the thiazole or selenazole substituent, depends on the structure of not only the substituents at the 1,4-benzoquinone nucleus, but also the hetaryl groups and substituents present in their composition. This confirms the presence of delocalization of the unpaired electron over the π-electron system of the hetaryl substituent. For example, replacement of a chlorine atom in the 5 position of 1,4-benzoquinone (I) by the N-methylpiperazyl group (II) increases the density of the unpaired electron in the π-electron system of the thiazole substituent, as expressed in an increase of both a_H and other HFS constants which determine the additional broadening of the ESR signals. The replacement in the thiazole substituent of the nitrogen atom in the $1s^2 2p^2 \sigma^2 \pi^1$ electronic state (I) by a positively charged nitrogen atom in the $1s^2 2\sigma^3 \pi^1$ state (VI) also increases the density of the unpaired electron in the heterocycle.

In contrast to the free radicals of 5-selenazolyl- (VII) and 5-thiazolyl-substituted benzoquinones (I-VI), the ESR spectra of 4-pyrazolyl-substituted benzoquinones (IX, X) do not show the interaction of the unpaired electron with a proton, and this can apparently be explained by the influence of the electron-donor properties of the nitrogen atom in the electronic state $1s^2 2p^2 \sigma^3$ adjacent to the CH fragment and preventing the delocalization of the unpaired electron on the CH fragment.

Below, one can similarly try to follow changes in the value of the HFS constant of the ESR spectra of the free radicals of the compounds studied, and thus, changes in the density of the unpaired electron in the free radical, as well as the electrophilicity of the CH fragment toward the unpaired electron in the initial molecule, but the absence of distinct series of the compounds studied makes it possible to detect qualitative effects only.

EXPERIMENTAL

The compounds studied were prepared by the following methods: I, III — [6], II — [7], IV — [2], V — [8], VI — [9], VII — [10], VIII — [11].

The free radicals were generated in the steady state on the surface of a flat platinum electrode in a cell placed in a type (H_{102}) rectangular cavity of an ER-9 ESR spectrometer (Carl Zeiss, Jena) according to the method described in [3].

The ESR spectra were recorded at a magnetic field scanning rate of 0.04 G/sec with a depth of high-frequency (100 kHz) modulation of a 0.05-G field and a recording time constant of 0.45 sec. The scanning of the magnetic field was calibrated against the ESR spectrum of the nitrobenzene anion radical [12]. The g-factor values of the free radicals were determined according to the method of [13]. For the electrochemical generation of the free radicals, use was made of $5 \cdot 10^{-5}$-$5 \cdot 10^{-4}$ mole/liter solutions of compounds I-X in anhydrous acetonitrile [14]; the solutions contained 0.1 mole/liter of tetrabutylammonium hexaflurophosphate.

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