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INTERMEDIATE PRODUCTS OF THE PHOTOREDUCTION

OF DIPHENOQUINONES

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O. B. Lantratova, V. A. Kuz'min, A. I. Prokof'ev, I. V. Khudyakov, and I. E. Pokrovskaya

Diphenoquinones are strong electron acceptors and can be reduced to semiquinone radicals. Ion-radical salts of diphenoquinones are organic conductors [1]. The photochemical reactions of the diphenoquinones have been studied because of the proposed application of these compounds in silver-free photography [2]. The diphenoquinones are strongly colored compounds which are reduced and decolorized when photoexcited in the presence of suitable donors [2, 3].

In the present work pulse photolysis and EPR have been used to investigate the spectral and kinetic characteristics of the semiquinones which represent intermediate products of the reduction of diphenoquinones



as well as the redox potentials of diphenoquinone/semiquinone pairs.

EXPERIMENTAL

Unsubstituted diphenoquinone (Q, X = H), 3,3',5,5'-tetrachlorodiphenoquinone (ClQ, X = Cl), 3,3',5,5'-tetrabromodiphenoquinone (BrQ, X = Br), and the corresponding dihydroxybiphenyls (QH₂, ClQH₂, and BrQH₂) were synthesized according to [4-6]. 1,4-Benzoquinone (B), recrys-tallized from ethanol and distilled under vacuum, and the Na salt of 2,6-disulfo-9,10-anthraquinone, recrystallized from aqueous ethanol, were also used in the present work. The solvents used were chromatographic-grade CH₃CN, C₆H₆, C₆H₅CH₃, C₂H₅OH, dibutyl phthalate, distilled under vacuum, D₂O, redistilled water, and redistilled glacial CH₃COOH. The solutions in H₂O--CH₃CN (1:1 by vol.) had a pH of 7.0 (borate-phosphate buffer, 10^{-2} M); the pH of the solutions was measured with a pH 340 potentiometer.

In order to prepare solvents with different viscosities, acidified CH_3CN was mixed with dibutyl phthalate. The viscosities of the solutions prepared were measured with a Hoeppler viscometer ($1.2 \le n \le 3.6$ cP). The working concentrations of the diphenoquinone solutions were 10^{-5} to 10^{-6} M, of the corresponding dihydroxybiphenyls 10^{-2} to 10^{-3} M.

The absorption spectra and breakdown kinetics of the intermediate products were recorded on a pulse photolysis apparatus [7]; photoexcitation was achieved through UFS-5 light filters $(\lambda 280-380 \text{ nm})$ and through a combination of light filters ZhS-10 and SS-8 ($\lambda 400-480 \text{ nm}$). When necessary, oxygen was removed from the solutions under vacuum. The EPR spectra of the solutions, free of oxygen, were obtained on a Varian E 12-A spectrometer with a thermostatted attachment; the solutions studied were irradiated in the resonator by the full light of a DRSh-1000 lamp. The radical concentrations were obtained by comparing the intensity of the EPR spectra of the samples with that of a standard (2,2,6,6-tetramethyl-4-piperidon-l-oxyl).

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Fig. 1. Absorption spectra of 1) ClQ, 3) ClQ⁻ in CH_3CN , and 2) ClQH^{*} in CH_3CN with 1% AcOH, taken in the pulse photolysis of solutions of ClQ and ClQH₂.

Fig. 2. Absorption spectra of 1) BrQ and 2) BrQ^{-} in CH_3CN , taken in the pulse photolysis of solutions of BrQ and $BrQH_2$.

The absorption spectra of the solutions were obtained on a Specord UV-VIS spectrophotometer. All tests, except those indicated in the text, were carried out at $20 \pm 1^{\circ}$ C.

DISCUSSION OF RESULTS

<u>Creation of Radicals, Absorption Spectra, and EPR Spectra.</u> The absorption spectra of Q, ClQ, and BrQ are shown in Figs. 1-3. In the case of pulsed photoexcitation of oxygenfree or air-saturated solutions of diphenoquinones in CH₃CN or in a mixture of CH₃CN and H₂O through a combination of ZhS-10 and SS-8 light filters no absorption to any intermediate products was observed. In the case of photoexcitation of diphenoquinone solutions in the presence of the corresponding dihydroxybiphenyls in the same solvents semiquinone radicals were formed (see Figs. 1-3) according to the reactions [3]

$$0 + hv \to 0_s^* \to 0_T^* \tag{1}$$

$$Q_T^* + QH_2 \rightarrow 2QH^*$$
⁽²⁾

$$0H^{\bullet} \rightleftharpoons 0^{-} + H^{+} \tag{3}$$

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The position of the equilibrium (3) depends on the basicity of the medium. In the above-mentioned solvents the QH[•], ClQ⁻, and BrQ⁻ radicals were formed (see Figs. 1-3). In the case of pulsed photoexcitation of dihydroxybiphenyls in the same solvents through the UFS-5 light filter no intermediate products were observed.

The introduction into the acetonitrile solution of C1Q and C1QH₂ of the stable radical (C $\leq 10^{-2}$ M)



lead to a decrease of the yield of the semiquinone radical; the value of the Stern-Volmer quenching constant was $K = (130 \pm 5)$ liters/mole. The decreased yield of the semiquinone radical was due to quenching by the stable radical of the electron-excited state of the dipheno-quinone, the precursor of the semiquinone [8]. Furthermore, $K = k_q\tau$, where k_q is the



Fig. 3. Absorption spectra of 1) Q, 2) QH[•] in CH_3CN , and 3) Q[±] in CH_3CN with 0.01 N NaOH. Spectra obtained in the pulse photolysis of solutions of Q and QH_2 .

Fig. 4. EPR spectrum of ClQH $^{\circ}$ obtained by the irradiation of the solutions of ClQ and ClQH₂ in toluene at 140 $^{\circ}$.

quenching rate constant and τ the lifetime of the excited state. The value of $k_q \leq 10^{10}$ liters/mole·sec; consequently, $\tau \geq 10^{-8}$ sec, i.e., the formation of the semiquinone proceeds with the participation of the triplet state of the diphenoquinone [Eq. (2)]. It must be pointed out that in the presence of 0_2 the yield and the kinetics of radical decay remain the same.

Aliphatic alcohols usually reduce the carbonyl groups of molecules existing in the triplet state. In fact, ClQ^{-} radicals were formed in the pulsed photoexcitation of ClQ solutions in ethanol (see Fig. 1).

In an alkaline medium (0.5 M KOH in CH₃CN) ClQ and BrQ were reduced in the dark to the corresponding radical-anions. A long-wave band (λ_{max} 750 nm for ClQ and λ_{max} 775 nm for BrQ) appeared in the absorption spectra of these solutions, due to the absorption of the radical-anion ClQ[±] and BrQ[±]. The absorption spectra of ClQ[±] and BrQ[±], recorded spectrophotometri-cally by the pulsed-photolysis method (see Figs. 1 and 2), practically coincide with respect to the position of the maxima and shape of the bands. The concentration of ClQ[±] and BrQ[±] remained the same in the alkaline medium for several hours. EPR spectra of ClQ[±] and BrQ[±] were recorded in the same solutions which represent a singlet (width between the points of maximum gradient 2 Oe). The EPR spectra and absorption spectra of the same solutions were recorded, which allowed us to determine the concentration of the radicals and, consequently, to assess the extinction coefficients $\varepsilon_{750} = (1.5 \pm 0.5) \cdot 10^4$ liters/mole cm (ClQ[±]) and $\varepsilon_{775} = (2.3 \pm 0.5) \cdot 10^3$ liters/mole cm (BrQ[±]).

The radical ClQH was formed in the pulsed photoexcitation of ClQ and ClQH₂ solutions in a mixture of CH₃CN and AcOH (AcOH content 1-100%). In the pulsed photoexcitation of ClQ







Fig. 6. Oscillogram of absorption changes at $\lambda = 750$ nm caused by the formation of decay of ClQ⁴. Data obtained in the pulsed photolysis of B and ClQH₂.

Fig. 7. E7' as function of EAabs.

and $ClQH_2$ solutions in CH_3CN and when this solution is acidified with AcOH (the concentrations of ClQ and $ClQH_2$ remaining constant) evidently the equal amounts of ClQ^{-} (CH_3CN) and $ClQH^{-}$ [acidified CH_3CN , see Eqs. (2) and (3)] are obtained. This allowed us to assess ε_{600} ($ClQH^{-}$) = (1.6 ± 0.5) $\cdot 10^{-4}$ liters/mole cm. The extinction coefficient for BrQH⁻ could not be determined, due to the poor solubility of BrQ.

The addition of NaOH to the solution of Q in CH_3CN did not lead to the formation of paramagnetic particles and the appearance of new bands in the long-wave region of the absorption spectrum of the solution. Apparently, Q polymerizes in an alkaline CH_3CN solution and under these conditions Q[±] is unstable. The absorption spectrum of Q[±] (see Fig. 3) was obtained in the pulsed photolysis of a freshly prepared solution of Q in CH_3CN , containing 0.01 M NaOH. The extinction coefficient of QH^{*} in CH_3CN was assessed from photooxidation experiments of 4,4'-dihydroxybiphenyl, sensitized with the Na salt of 2,6-disulfo-9,10-anthraquinone, according to [9]: ε_{575} (QH^{*}) = (5.1 ± 0.5) ·10³ liters/mole·cm. In a weakly alkaline CH_3CN solution the value of ε_{800} (Q[±]) = (7.5 ± 0.5) liters/mole·cm was obtained in the same way as the ε value for (C1QH^{*}) (see above).

According to the well-known rule for quinones, a gradual shift of the long-wave absorption maximum of the particle towards the red region takes place in the transition diphenoquinone \rightarrow neutral semiquinone \rightarrow radical-anion (see Figs. 1-3) [10]. The absorption spectra of the three diphenoquinones are very similar, which is also true for the radicals (see Figs. 1-3).

It was not possible to record the EPR spectra of radicals in the irradiation of toluene solutions of the diphenoquinones and the corresponding dihydroxybiphenyls in the resonator of the EPR spectrometer. When the temperature was increased to $\sim 130-140^{\circ}$, the EPR spectrum of the neutral semiquinone radical ClQH[•] (Fig. 4) was obtained, which is formed according to the reaction

$$ClQ + ClQH_2 \stackrel{\Delta}{=} 2ClQH$$
 (4)

The spectrum represents a quintuplet with a binomial intensity ratio, caused by the interaction of the unshared electron with four equivalent ring protons ($a_{\rm H} = 1.8$ Oe). Each component of the quintuplet contains seven lines (1:2:3:4:3:2:1), the appearance of which is due to the interaction of the unshared electron with the magnetic isotopes ³⁵Cl and ³⁷Cl (I = 3/2), located in the o position with respect to the univalent O atom ($a_{\rm Cl} = 0.85$ Oe). This treatment of the spectrum is in full agreement with the data obtained for p-phenyl-substituted phenoxyls [11]. The EPR spectra for some neutral semiquinone radicals, formed according to reaction (4), have been obtained earlier [12]. The absence of the hfs of the hydroxyl proton must be pointed out. In order to confirm this finding, D₂O was added to the system, which usually participates in a H-D exchange with the hydrogen of the neutral semiquinone [13, 14]. However, no changes in the EPR spectrum were observed. The EPR spectra of BrQH' radicals could not be recorded, due to poor solubility of BrQ and BrQH₂ and instability of the radical. The C-Br bond is relatively weak, so that at high temperatures the radicals corresponding to BrQ decompose with the evolution of bromine.

Kinetics of Radical Decay. The decay of ClQH' radicals in AcOH and in a mixture consisting of acidified CH₃CN and dibutyl phthalate, and of QH' radicals in CH₃CN obeys a secondorder kinetic law:

$$(Cl)QH' + (Cl)QH' \rightarrow (Cl)Q + (Cl)QH_2$$
(5)

The values of $2k_5$ obtained for ClQH[•] in AcOH and for QH[•] in CH₃CN were equal to $(1.7 \pm 0.6) \cdot 10^9$ and $(5.6 \pm 0.6) \cdot 10^8$ liters/mole·sec, respectively. The $2k_5$ values obtained for ClQH[•] are identical within the limits of experimental error to $1/4k_{diff}$, calculated by the Debye equation for AcOH and the above solvent mixture. This means that the disproportionation of ClQH[•] as well as of the related 2,6-diphenyl-4-(3',5'-diphenyl-4'-hydroxyphenyl)phenoxyl radicals is limited by progressive diffusion [3]. These radicals do not contain three-dimensional bulky substituents around the reaction center and the anisotropy of the reactivity of these particles is fully centralized during the encounter. The $2k_5$ value obtained for QH[•] is lower by about one order of magnitude than 1/4k for CH₃CN. It is possible that the disproportionation of this radical takes place in the kinetic region.

The decay of ClQ⁻ in the C_6H_6 -CH₃CN mixture (CH₃CN content 50-100%) strictly obeys a first-order kinetic law. The decay rate of ClQ⁻ increases with increasing CH₃CN content of the mixture (Fig. 5). Evidently, ClQ⁻ interacts with CH₃CN with the formation of an acianion

$$ClQ^{-} + CH_3CN \rightarrow ClQH' + [CH_2CN]^-$$
 (6)

The data in Fig. 5 gave $k_6 = (4.4 \pm 0.1)$ liters/mole.sec. BrQ- decays probably, following an analogous reaction. Its decay in CH₃CN also strictly follows a first-order kinetic law. However, due to poor solubility of BrQ and BrQH₂ in the presence of benzene we were not able to measure k_6 . The disproportionation of Q- in a weakly alkaline CH₃CN solution follows a second-order kinetic law:

$$Q^{-} + Q^{-} \to Q + Q^{2^{-}} \tag{7}$$

 $2k_7 = (9.2 \pm 0.6) \cdot 10^7$ liters/mole.sec.

<u>One-Electron Redox Potentials of Diphenoquinones.</u> One-electron potentials E_{7}^{1} of the pairs ClQ/ClQ⁻ and BrQ/BrQ⁻ were measured in a H₂O--CH₃CN medium (pH 7.0) in experiments with a "quinone for comparison" B [E_{7}^{1} (B/B⁻) = +0.099 V] [15]. E_{7}^{1} was determined using the following procedure. Equal concentrations of B⁻ and Cl(Br)Q⁻ are formed in the pulsed photo-excitation of B (10⁻⁴ to 10⁻⁵ M) through a UFS-5 light filter in the presence of an excess of dihydroxybiphenyl Cl(Br)QH₂ (10⁻²-10⁻³ M) according to the reaction $B + hv \rightarrow Bs^* \rightarrow B_T^*$

$$B + hv \rightarrow B_{S}^{+} \rightarrow B_{T}^{+}$$

$$B_{T}^{*} + Cl(Br)QH_{2} - B^{-} + Cl(Br)Q^{-} + 2H^{+}$$
(8)
(9)

Only C1(Br)Q⁻ absorbs when $\lambda > 500$ nm. After the flash a decrease of the C1(Br)Q⁻ concentration to the equilibrium value is observed (Fig. 6), due to the reaction

$$Cl(Br)Q^{-} + B \rightleftharpoons Cl(Br)Q + B^{-}$$
 (10)

The oscillograms of spectral changes (see Fig. 6) were used to obtain the values of $[ClQ^{\perp}]_0$, i.e., the concentrations of ClQ^{\perp} at the moment after the flash, and of $\overline{[ClQ^{\perp}]}$, the equilibrium concentration of ClQ^{\perp} , calculated from the signal on the plateau of the oscillogram. In order to obtain the values of E_7^1 of the diphenoquinones, it is necessary to know K_{10} [16]:

$$K_{10} = \frac{[\overline{B}^{\perp}][\overline{ClQ}]}{[\overline{ClQ}^{\perp}][B]} = \frac{(2[\overline{ClQ}^{\perp}]_0 - [\overline{ClQ}^{\perp}])([\overline{ClQ}^{\perp}]_0 - [\overline{ClQ}^{\perp}])}{[\overline{ClQ}^{\perp}][B]}$$

where $[\overline{B^{\perp}}]$ is the equilibrium concentration of B^{\perp} and [B] is the initial concentration of B; $[B] \gg [\overline{B^{\perp}}]$.

The redox potential E_7^1 can be calculated from the equation [16]:

$$E_{7}^{1}(\text{ClQ/ClQ}^{-}) = E_{7}^{1}(\text{B/B}^{-}) - 0.059 \text{ lg}K_{10}$$

The value obtained for E_7^+ (ClQ/ClQ[±]) = (0.26 ± 0.01) V. The value of E_7^+ (BrQ/BrQ[±]) = (0.26 ± 0.01) V was obtained in the same way. The method used was checked by determining E_7^+ (ClQ/ClQ[±]) by the method described, i.e., by measuring the rate of decrease of the ClQ[±] concentration down to the equilibrium concentration [16, 17]. For this purpose pulsed photoexcitation was carried out on the "quinone-for-comparison" solutions and solutions of ClQ, using exactly known concentrations, with a donor (ethanol) concentration of 10^{-3} M. The [B]/[ClQ] ratio was 4:80. The value of E_7^+ , calculated from kinetic measurements was E_7^+ (ClQ/ClQ[±]) = (0.26 ± 0.02) V; it coincided within the limits of experimental error with E_7^+ , calculated from equilibrium concentrations. Thus, the E_7^+ characterize ClQ and BrQ as exceptionally strong electron acceptors of the quinone series. The highest value of E_7^+ = 0.099 V was obtained for 1,4-benzoquinone [15].

Quinones are widely used as electron acceptors. According to literature data and data obtained in the present work, the redox potentials of quinones in aqueous solutions or in aqueous solutions containing polar organic solvents vary within very wide limits: from -0.375 V (Na salt of 2-sulfoanthraquinone) [15] to 0.26 V (ClQ and BrQ). This allows us to select a quinone with a known potential and to calculate the equilibrium concentrations in redox systems which contain quinones and to predict the route of some redox reactions.

It is of great interest to compare the known E_1^2 values of quinones with other parameters that characterize their acceptor capacity. For a very large number of quinones the literature contains EA_{abs} values, i.e., the absolute electron affinity [18]. EA_{abs} and E_7^2 characterize the acceptor properties of the molecules in the gaseous phase and in an aqueous organic phase, respectively. In the absence of solvation effects the graphical relationship between the electron affinity and the reduction potential must be a straight line with a tangent of the slope angle equal to unity [19]. Figure 7 shows that the values of EA_{abs} and E_7^2 change symbatically; however, the tangent of the slope angle is equal to 0.5. In the case of nitroaromatic compounds the corresponding value is 0.2 [19], i.e., solvation of the acceptors by polar molecules decreases their electron affinity.

CONCLUSIONS

1. In the photoexcitation of diphenoquinone solutions in the visible region in the presence of the corresponding biphenyls semiquinone radicals are formed. The reaction proceeds with the participation of the triplet state of the diphenoquinone.

2. The absorption spectra have been recorded and the extinction coefficients calculated of neutral semiquinone radicals and radical-anions.

3. The EPR spectra of radical-anions represent singlets. The EPR spectrum of the semiquinone radical of tetrachlorodiphenoquinone represents a quintuplet with a binomial ratio of the intensities.

4. Disproportionation of the ClQH⁻ radicals is limited by progressive diffusion.

5. The values of the one-electron redox potentials of the pairs C1Q/C1Q⁻ and BrQ/BrQ⁻ have been determined. The acceptor properties of the quinone molecules are less pronounced in an aqueous organic medium than in the gaseous phase.

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EFFECT OF π -ELECTRON CONJUGATION OF THE CHROMOPHORES ON THE REACTIVITY OF THE TRIPLET STATES OF DYES WITH TWO CHROMOPHORES IN ELECTRON-TRANSFER REACTIONS

Yu. E. Borisevich, V. A. Kuz'min, and I. V. Renge UDC 541.124:541.651.22:541.42

Conjugation of the chromophores has a considerable effect on the spectral and kinetic characteristics of the singlet and triplet states of cyanine dyes with two interacting chromophores [1, 2]. The triplet (T) states of cyanine dyes are deactivated in the presence of electron donors or acceptors by a mechanism of charge-transfer complex (CTC) formation between the triplet molecule and the quenching agent [3] or by complete transfer of an electron [4].

In the present work the dependence has been studied of the quenching efficiency of the T states of various cyanine dyes with two chromophores (biscyanines) by electron donors and acceptors on the degree of π -electron conjugation of the chromophores.

EXPERIMENTAL

The studies were carried out in a pulse photolysis apparatus [5] according to the procedure given in [6]. The homologous series of alcohols were used as solvents. The triplet states were generated either directly by photoexcitation or by T-T transfer of the triplet energy from a donor (anthracene). The oxidation and reduction potentials of the dyes were measured in methanol at $\sim 20^{\circ}$ C with respect to a saturated calomel electrode. Oxidation potentials ($E_{\rm OX}$) were measured at a rotating glass-graphite electrode (n = 1400 rpm); the reduction potentials ($E_{\rm red}$), at a dropping Hg electrode by the standard method [7]. The dyes with two chromophores were synthesized in the Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSSR, and were purified by double recrystallization.

DISCUSSION OF RESULTS

In a number of bis-dye isomers [i.e., dyes differing only in the spatial structure of the central heterocyclic group (Fig. 1): series A, (I)-(IV); series B, (V)-(IX); series C, (X)-(XII); series D, (XIII)-(XIV)], a general longwave shift is observed of the bands of the singlet-singlet absorption spectrum due to π -electron conjugation of the dye chromophores via the central heterocyclic system [1]. The longwave shift increases with increase in the degree of π -electron conjugation of the chromophores. In turn, the magnitude of the longwave shift of the absorption spectrum in a series of dye isomers can be characterized by the value of the average energy of the S₁* + S₀ transitions of the bis-dyes

$$E_{avi} = \frac{E_{1i} - E_{2i}}{2}$$
(1)

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