Electron transfer and paramagnetic products of reactions of haloquinones with aliphatic amines

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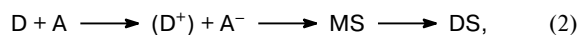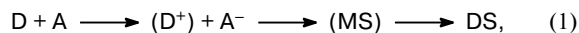[b]*Kazan State Technological University, 68 ul. K. Marksa, 420015 Kazan, Russian Federation. E-mail: nefediev@ kstu.kcn.ru*

The reactions of chloranil (Cl_4Q) and bromanil (Br_4Q) with aliphatic amines in a DMF : H_2O (5 : 1, vol/vol) mixture were studied. The radical anions of 2,5-didimethylamino-3,6-chloro-*p*-benzoquinone and 2,5-didimethylamino-3,6-bromo-*p*-benzoquinone were identified by ESR spectra. The reaction rate constant of the replacement of two chlorine atoms by the amino groups in the radical anion of Cl_4Q at 288 K was estimated.

Key words: chloranil, bromanil, dimethylamine, diethylamine, 2,5-didimethylamino-3,6-chloro-*p*-benzoquinone, 2,5-didimethylamino-3,6-bromo-*p*-benzoquinone, *N,N*-dimethylformamide, free radicals, ESR spectroscopy, electron transfer.

Interaction of amines with quinones is a typical reaction between electron donors and acceptors.[1—4] The reactions of various aliphatic amines with *p*-benzoquinone and its chlorine-substituted derivatives have been studied[5—8] by rapid-scanning spectrophotometry. The kinetics of formation of the intermediates and final products was studied in the system containing *n*-butylamine and chloranil in solutions of EtOH and Et_2O. Five types* of the reactions were distinguished on the basis of the data obtained for the reactions of various aliphatic amines (D) with *p*-benzoquinone and its chloro derivatives (A):

$$D + A \longrightarrow (D^+) + A^- \longrightarrow (MS) \longrightarrow DS, \quad (1)$$

$$D + A \longrightarrow (D^+) + A^- \longrightarrow MS \longrightarrow DS, \quad (2)$$

$$D + A \longrightarrow (D^+) + A^-, \quad (3)$$

$$D + A \longrightarrow MS \longrightarrow DS, \quad (4)$$

$$D + A \longrightarrow (MS) \longrightarrow DS. \quad (5)$$

Here D and A are the electron donor and acceptor, D^+ and A^- are the radical cation and anion of the donor and acceptor, and MS and DS are the 2-mono- and 2,5-disubstituted products.

In this work, we studied the mechanism of the reaction of halogenquinones with aliphatic amines in a DMF—H_2O (5 : 1) mixture.

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* Hereafter the formulas of species, whose spectra are not observed, are given in parentheses.

Experimental

Chloranil (Cl_4Q) and bromanil (Br_4Q) were purified by recrystallization and sublimation under reduced pressure. Aqueous solutions (33%) of Me_2NH (7.3 mol L^{-1}) and Et_2NH (4.5 mol L^{-1}) were used. Solutions of Cl_4Q and Br_4Q were prepared in DMF (10^{-3} mol L^{-1}) and mixed with a 33% aqueous solution of amine (the DMF : H_2O ratio in the resulting solution was 5 : 1). Dissolved oxygen was removed from solutions by the triple freezing—evacuation—thawing out cycle. Gaseous oxygen was bubbled through a solution of Br_4Q in DMF for 5 min to saturate the solution with oxygen.

ESR spectra were recorded on a Bruker-ER200D radio-spectrometer (Germany) equipped with a B-VT-1000 temperature controller. The error of determination of absolute concentrations was 30%.

HFC constants were determined by plotting of the theoretical isotropic spectra and fitting to experiment assuming the Lorentz shape of lines.

Results and Discussion

Time-resolved ESR spectra of the products of the reaction of Cl_4Q with Me_2NH are presented in Fig. 1. Amines were introduced in excess amounts to maintain their concentration nearly constant in the course of the reaction.

The ESR spectrum exhibits the signal from the $Cl_4Q^{•-}$ radical anion (intense central line) and the much lower-intensity signal of the $Me_2NO^{•}$ dimethylnitroxyl radical. The magnetic resonance parameters of the paramagnetic
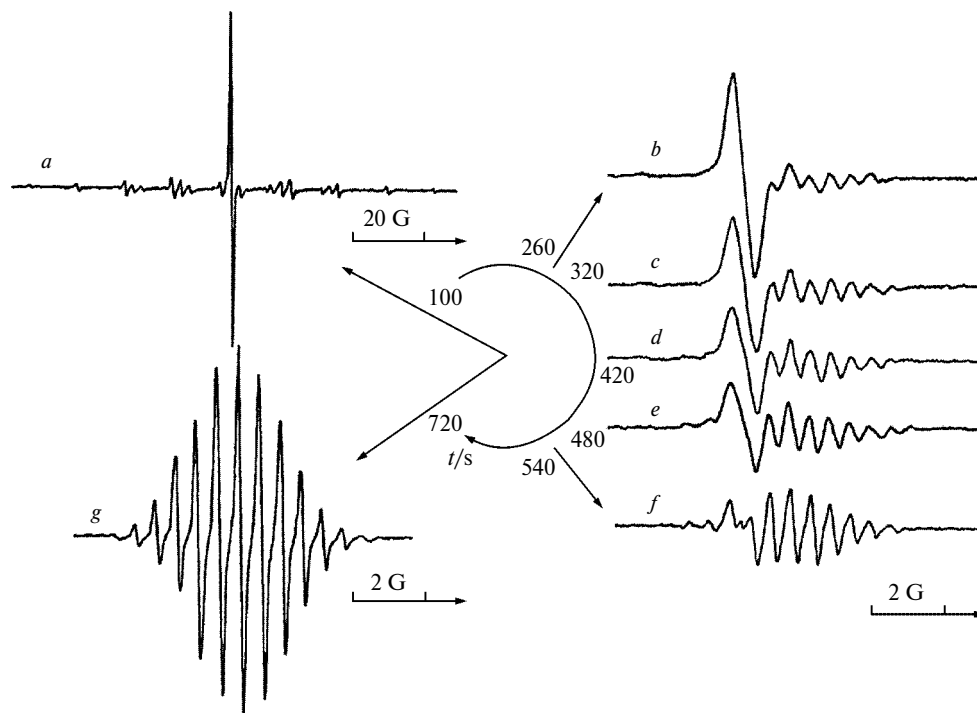
Fig. 1. Time-resolved ESR spectra for the $Cl_4Q–Me_2NH$ system in a $DMF–H_2O$ (5 : 1) solution at 288 K. Concentration of the initial Cl_4Q is $\sim 1 \cdot 10^{-3}$ mol L^{-1}, $[Me_2NH]$ is ~ 7.3 mol L^{-1}. The time after mixing of the components (t) is shown around the circle.

intermediates and products are presented in Table 1. The appearance of these signals indicates the primary prevailing electron transfer from the Me_2NH donor to the Cl_4Q acceptor (Scheme 1).

Scheme 1
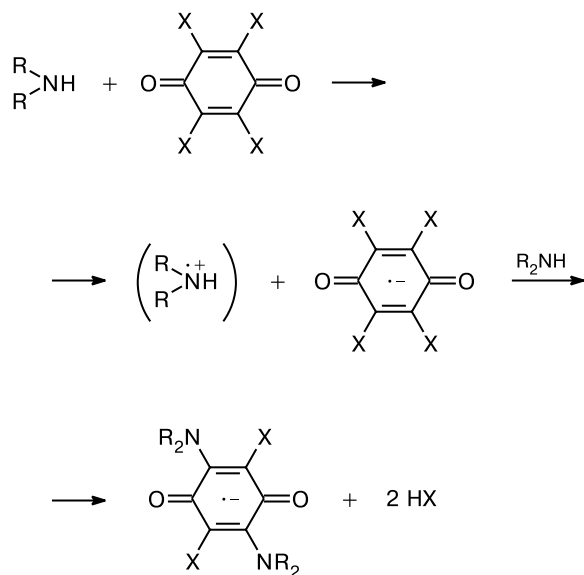
R = Me, Et   X = Cl, Br

Table 1. Magnetic resonance parameters of the paramagnetic intermediates and reaction products

Paramagnetic species	R or X	HFC constant/G (±0.2 G)		g-Factor (±0.0001)
		a_N	a_H	
$\overset{\cdot}{O}-N{<}^R_R$	Me	16.0	13.5	2.0060
	Et	16.2	10.8	2.0061
[quinone structure]	Cl	—	—	2.0060
	Br	—	—	2.0088
[Me₂N substituted quinone]	Cl	0.6	0.6	2.0052
	Br	0.5	0.5	2.0059

The $Cl_4Q^{\cdot -}$ radical anion is observed directly in the ESR spectrum, whereas the $Me_2N^{\cdot +}H$ radical cations are very reactive, so their ESR spectra are not detected. The appearance of the ESR spectrum of $Me_2NO^{\cdot}$ is a result, most likely, of reactions of the aminyl radical[9] and amine with molecular oxygen dissolved in the system under study (Scheme 2). Then the intensity of the signal from the radical anion decreases, and the ESR spectrum of a new species appears in a higher field. The $Me_2NO^{\cdot}$ free radi-
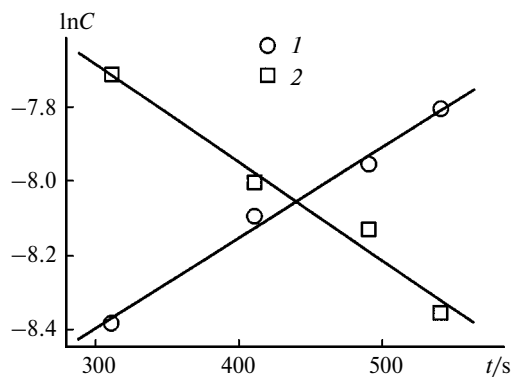
**Fig. 2.** Changes in time of the concentrations (C) of $Cl_4Q^{\bullet-}$ (*1*) and $1^{\bullet-}$ (*2*) in the semilogarithmic coordinates during the reaction of Cl_4Q with Me_2NH (*t*).

cal is unstable in this medium, and its spectrum disappears soon (see Fig. 1, *b*). The intensity of the new spectrum increases in time to an extent to which the intensity of the signal from the radical anion decreases (see Fig. 1, *c—f*), so that it completely replaces the latter (see Fig. 1, *g*). Based on the ratio of intensities and the number of lines, we can attribute the new spectrum to the radical anion of 2,5-di(dimethylamino)-3,6-dichloro-*p*-benzoquinone ($1^{\bullet-}$). The signal of the monosubstituted product is absent. In a $DMF—H_2O$ (5 : 1) solvent mixture, the reaction of $Cl_4Q^{\bullet-}$ with Me_2NH affords disubstituted radical anion $1^{\bullet-}$.

Scheme 2
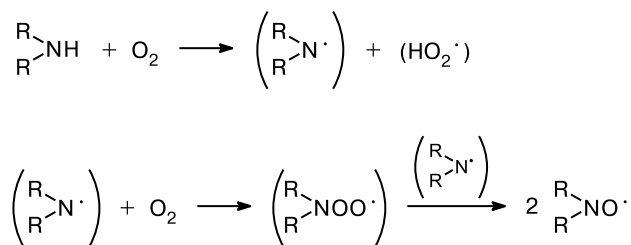
Aimed at revealing the reaction mechanism, we determined from the ESR spectra (see Fig. 1, *c—f*) the rate constant of substitution of $Cl_4Q^{\bullet-}$. The kinetics of pseudo-
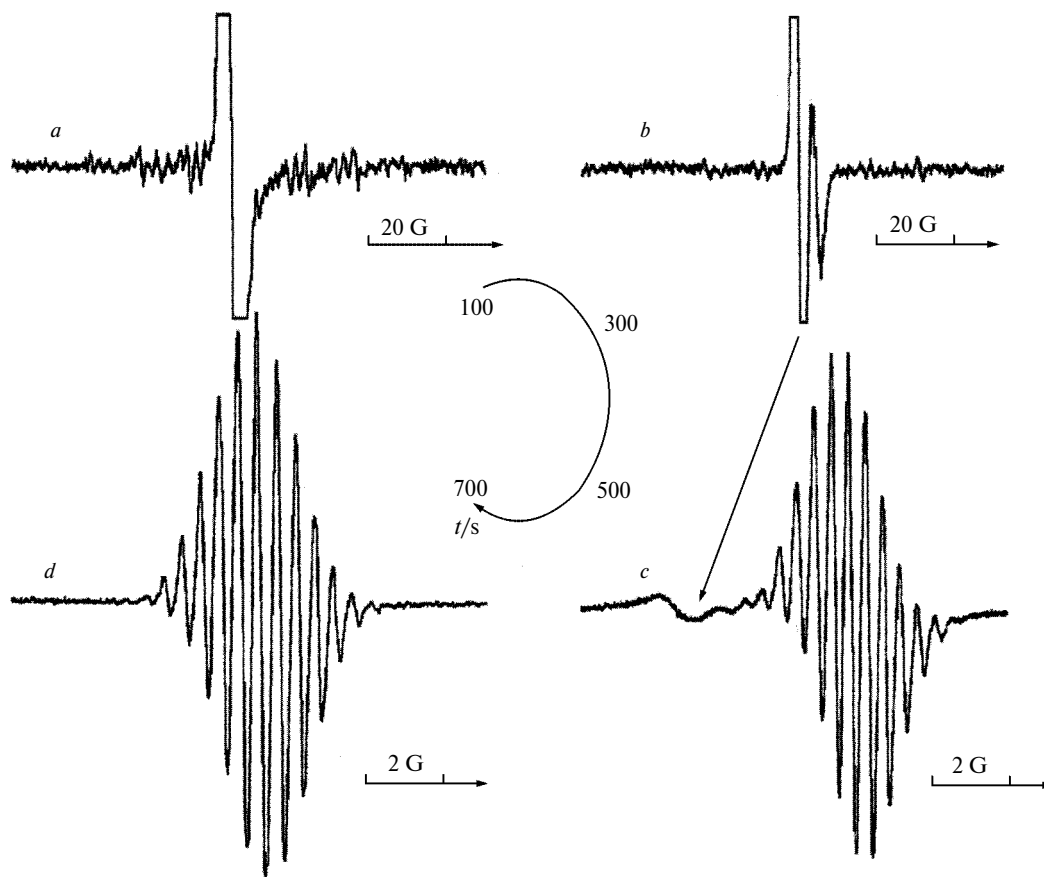
Fig. 3. Time-resolved ESR spectra for the $Br_4Q—Me_2NH$ system in a $DMF—H_2O$ (5 : 1) solution at 288 K. Concentration of the initial Br_4Q is ~$1 \cdot 10^{-3}$ mol L^{-1}, [Me_2NH] is ~7.3 mol L^{-1}. The time after mixing of the components (*t*) is shown around the circle.

first-order reactions at a high concentration of Me_2NH is described by the equation

$$d\ln[Cl_4Q^{\cdot-}] = kdt,$$

where $[Cl_4Q^{\cdot-}]$ is the concentration of the chloranil radical anion. The plots of $\ln[Cl_4Q^{\cdot-}]$ and $\ln[\mathbf{1}^{\cdot-}]$ *vs.* reaction time *t* are linear for both $Cl_4Q^{\cdot-}$ (line with a positive slope) and product $\mathbf{1}^{\cdot-}$ (line with a negative slope) (Fig. 2). The absolute values of slopes of the straight lines coincide, confirming that the assumed mechanism is valid. The rate constant of 2,5-disubstitution of the Cl atoms of the chloranil radical anions by dimethylamine at 288 K is $k = (2.6\pm0.3)\cdot10^{-3}$ L mol^{-1} s^{-1}. The relative error of the reaction rate constant is smaller than that of the absolute concentrations, and the relative concentrations of the paramagnetic species are sufficient for the calculation of rate constants.

ESR spectra of the Br_4Q-Me_2NH system in the same medium at different times after mixing of the reactants are presented in Fig. 3. The reaction mechanism is the same as that for Cl_4Q-Me_2NH (see Scheme 1, R = Me, X = Br). After the fast primary electron transfer, the $Br_4Q^{\cdot-}$ and $Me_2N^{\cdot+}H$ species are formed followed by the formation of the $Me_2NO^{\cdot}$ free radicals (see Scheme 2). The 2,5-disubstitution of the Br atoms in the $Br_4Q^{\cdot-}$ radical anion affords radical anion $\mathbf{2}^{\cdot-}$ (magnetic resonance parameters of the paramagnetic species are presented in Table 1).

The removal of and enrichment in oxygen of the solutions under study do not basically change the character of the reactions. In the first case, the nitroxyl radical does not appear. In the second case, the amount of the nitroxyl radical formed increases, and the radical is retained and coexists with the final product (Fig. 4).

Thus, we found one more mechanism in which some intermediates and the reaction product in a polar medium are stable radicals.

$$D + A \longrightarrow (D^{\cdot+}) + A^{\cdot-} \longrightarrow (DS)^{\cdot-}$$
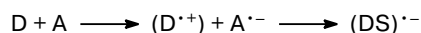
$D = Me_2NH$; $A = Cl_4Q$, Br_4Q

ESR spectrum of the Cl_4Q-Et_2NH system in a $DMF-H_2O$ (5 : 1) mixture (Fig. 5) contains signals from paramagnetic species of two types: the $Cl_4Q^{\cdot-}$ radical anion (intense central line) and the $Et_2NO^{\cdot}$ diethylnitroxyl radical. Magnetic resonance parameters of these species are presented in Table 1. The reaction occurs *via* Schemes 1 (R = Et, X = Cl) and 2. Unlike the above mechanisms in which dimethylamine is an electron donor, in this mechanism no addition to $Cl_4Q^{\cdot-}$ occurs, which is probably due to high steric hindrances from the ethyl substituents in the diethylamine molecule.

The geometrical parameters of 2,5-di(dimethylamino)-3,6-dichloro-*p*-benzoquinone and the corre-
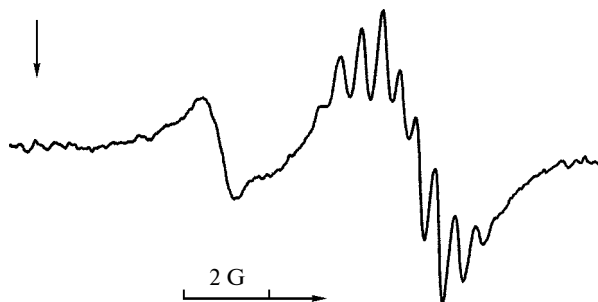
Fig. 4. ESR spectrum for the Br_4Q-Me_2NH system in a $DMF-H_2O$ (5 : 1) solution enriched in oxygen. Concentration of the initial Br_4Q is ~$1\cdot10^{-3}$ mol L^{-1}, $[Me_2NH]$ is ~7.3 mol L^{-1}. The fragment of the signal from the dimethylnitroxyl radical is shown by arrow.
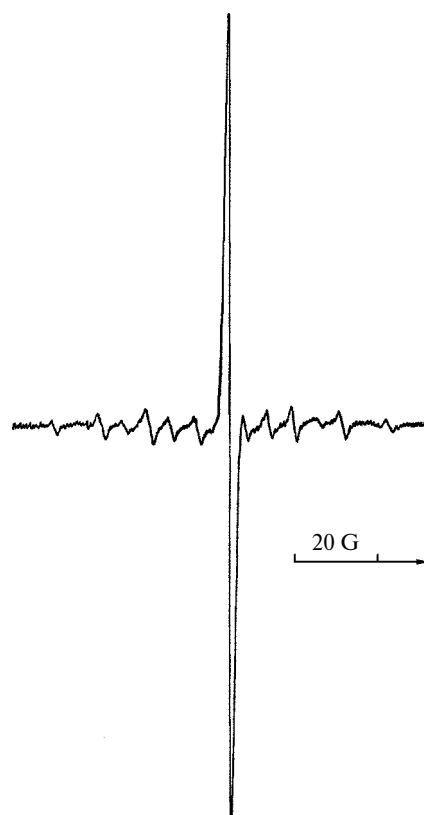
Fig. 5. ESR spectrum for the Cl_4Q-Et_2NH system in a $DMF-H_2O$ (5 : 1) solution at 288 K. Concentration of the initial Cl_4Q is ~$1\cdot10^{-3}$ mol L^{-1}, $[Et_2NH]$ is ~4.5 mol L^{-1}.

sponding radical anion and spin populations of the orbitals of the radical anion were calculated by the semiempirical method (UHF with the AM1 Hamiltonian). The isotropic HFC constant of magnetic moments of the unpaired electron and ^{14}N nucleus calculated from the found spin density values is ~0.33 G and has the same order of magnitude that the experimental value (isotropic coupling constant of the s-electron with

the ^{14}N nucleus equal[10] to 552 G was used in the calculation).

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