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Disproportionation of 2,5-Dichlorosemiquinone Radicals in Benzene According to Unsteady-State Kinetic Data for the Chain Reaction between 2,5-Dichlorohydroquinone and *N*,*N*'-Diphenyl-1,4-Benzoquinone Diimine

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Abstract—A method for determining the rate constant of disproportionation of 2,5-dichlorosemiquinone radicals (k_6) from unsteady-state kinetic data for the initiated chain reaction of *N*,*N*'-diphenyl-1,4-benzoquinone diimine with 2,5-dichlorohydroquinone have been developed, and two variants of this method are presented. The method is based on the study of the unsteady-state disappearance kinetics of one of the initial reactants (quinone diimine) in its initiated chain reaction with hydroquinone. The unsteadiness of the reaction is due to the presence of semiquinone radicals or initiator radicals accumulated before the start of the reaction at a concentration exceeding the steady-state concentration of semiquinone radicals in the chain reaction. The variants of the method differ in the order of mixing the reactants and initiator, on which the nature and concentration of the radicals accumulated in the system before the reaction depend. In the first variant, a quinone diimine + initiator solution is initially prepared and initiator radicals are accumulated. Hydroquinone is added to this solution (start of the reaction). In the second variant, a hydroquinone + initiator solution is initially prepared and semiquinone radicals from hydroquinone are accumulated. Quinone imine is then added to the solution (start of the reaction). The disproportionation rate constant of semiquinone radicals (k_6) is derived from the dependence of the decrease in the quinone imine concentration in a certain short time (~20 s) after the start of the reaction on the initiation rate. The rate constant k_6 in benzene is $(7.3 \pm 3.7) \times 10^6$ l mol^{-1} s^{-1} according to the first variant of the method and $(5.0 \pm 2.2) \times 10^6$ l mol^{-1} s^{-1} according to the second one.

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Kinetic studies of reversible chain reactions of quinone imines with hydroquinones provide data on the reactivity of stable participants of the reaction and intermediate semiquinone radicals [1, 2]. New possibilities were opened up by investigation of the unique chain reaction between *N*,*N*'-diphenyl-1,4-benzoquinone diimine (QDI) and 2,5-dichlorohydroquinone ($Ar(OH)_2$) [3]. This reaction has very long chains (10^4–10^5 units), due to which the reaction can be studied at initiation rates from 10^{-11} to 10^{-10} mol l^{-1} s^{-1}. The existence of a very sensitive method of quinone diimine analysis makes it possible to carry out studies at low concentrations of the reactants ($\leq 10^{-4}$ mol/l). In the absence of an initiator, the reaction has a well-defined autoacceleration period, which is due to the fact that the steady-state concentrations of the radicals are reached in a long time [3, 4]. The kinetics of the reaction in the presence of an initiator depends on the order of mixing the reactants and initiator [4]. Unsteady-state kinetic data for the initiated reaction of QDI with $Ar(OH)_2$ were earlier used to determine the disproportionation rate constant of 2,5-dichlorosemiquinone radicals $Ar(OH)O^{\bullet}$ [4]. The value thus obtained, $k = (5.8–7.1) \times 10^6$ l mol^{-1} s^{-1} (chlorobenzene, 298 K), is well below the value of ~10^8 l mol^{-1} s^{-1} presented for the reactions of other semiquinone radicals [5].

This work is devoted to the kinetics of the reaction between QDI and $Ar(OH)_2$ and to the determination of the disproportionation rate constant of the $Ar(OH)O^{\bullet}$ radical in benzene by the new unsteady-state kinetic method based on investigation of the initiated chain reaction between QDI and $Ar(OH)_2$ [4]. Benzene, chosen to be the solvent, is similar in properties to chlorobenzene, so we expected to obtain a k value close to the value obtained earlier. In this work, we developed and used a new (second) variant of the method of k determination based on the unsteady-state kinetics of the chain reaction of QDI with

$Ar(OH)_2$ [4]. Some of the results thus obtained are briefly presented in [6].

Interest in reversible chain reactions of quinone imines with hydroquinones is largely due, to their great practical significance. They are models of reactions of quinones with hydroquinones, which are very significant for chemistry and biochemistry because they determine the mechanism of the protective effect of quinone-type bioantioxidants (ubiquinones and group K vitamins) [7]. In addition, quinones and quinone imines are products of the oxidative degradation of the most popular antioxidants, namely, phenols (including hydroquinones) and aromatic amines [7–10]. The reactions of quinones and quinone imines under these conditions substantially affect the total antioxidation efficiency of the antioxidants.

EXPERIMENTAL

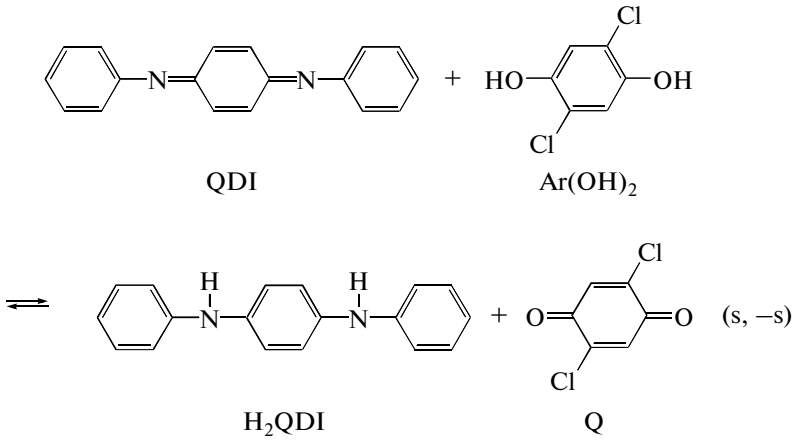
The synthesis and purification of QDI, $Ar(OH)_2$, *N*,*N*'-diphenyl-1,4-phenylenediamine (H_2QDI), 2,5-dichloroquinone (Q), and tetraphenylhydrazine (TPH) as an initiator were described previously [2–4]. Benzene was purified in the same way as chlorobenzene [3]. The reaction kinetics was studied as QDI disappearance. Experiments were carried out at 298 ± 0.1 K in a temperature-controlled quartz bubbler-type reactor cell (volume of 6.5 ml, path length of $l = 2.0$ cm, argon bubbling) built in a Specord UV VIS spectrophotometer coupled to a computer. The absorbance of the solution at $\lambda = 450$ nm ($\varepsilon = 7100$ l mol^{-1} cm^{-1}), 500 nm ($\varepsilon = 3910$ l mol^{-1} cm^{-1}), or 526 nm ($\varepsilon = 1680$ l mol^{-1} cm^{-1}) was recorded at different initial QDI concentrations at 1 s intervals. Although 2,5-dichloroquinone, one of the reaction products, is slightly absorbing in this region, its absorbance was neglected because of the small molar extinction coefficient ($\varepsilon_Q^{450} \approx 20$ l mol^{-1} cm^{-1}). The value of $k_i = 3.91 \times 10^{-7}$ s^{-1}, measured earlier in chlorobenzene [11], was accepted for the initiation rate constant in the decomposition of the TPH initiator at 298 K.

Since the reaction kinetics depends on the order of mixing the reactants and initiator in the reactor [12], we adhered to certain rules when conducting the experiments. Most experiments were performed according to the following procedure. The solvent was first loaded into the reactor, and solutions of QDI and the initiator were then added. Thereafter, argon was bubbled through the solution for a few minutes and a solution of $Ar(OH)_2$ was then added. After stirring the solution, QDI disappearance measurements were begun. Because some time was spent on adding the solution of the last reactant $Ar(OH)_2$, subsequent stirring, mounting a condenser on the reactor cell, and closing the cell compartment, we began QDI disappearance measurements not immediately, but, on the average, 20 ± 3 s after the addition of $Ar(OH)_2$. This time was taken into account in data processing.

In the second variant of *k* determination, the solvent and $Ar(OH)_2$ and initiator solutions were first placed in the reactor. Thereafter, argon was bubbled for 7–10 min [12], a solution of QDI was then added, and absorbance measurements were started after stirring. The time correction (20 ± 3 s) was again applied in data processing. For the changes in the starting concentrations of the reactants and radicals due to the addition of the solution of the second reactant to be ignorable, the volume of the latter was set to be 0.6–0.7 ml or below.

RESULTS AND DISCUSSION

The reaction between QDI and $Ar(OH)_2$ obeys the stoichiometric equation



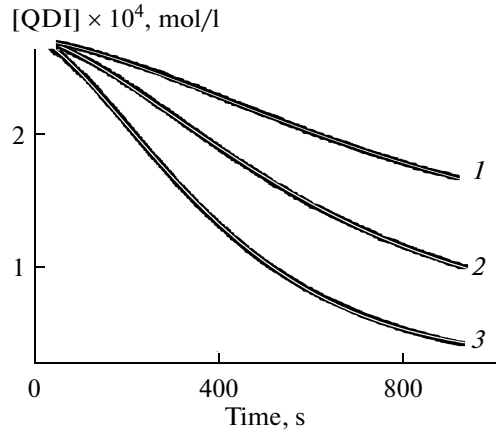


Fig. 1. QDI disappearance kinetics in the chain reaction with $Ar(OH)_2$ at $[Ar(OH)_2]_0 = (1)\ 1.8 \times 10^{-4}$, (2) 2.7×10^{-4}, and (3) 3.6×10^{-4} mol/l. $[QDI]_0 = \text{const} = 2.7 \times 10^{-4}$ mol/l; benzene as the solvent; $\lambda = 526$ nm; $T = 298$ K. Black points represent experimental data, and white lines represent the data calculated via Eq. (1). Experimental values of the parameters: curve *1*: $a = (1.52641 \pm 0.00084) \times 10^{-4}$ mol/l, $b = (-0.42378 \pm 0.00453) \times 10^{-4}\ s^{-c}$, $c = 1.49085 \pm 0.00164$, $d = (11.62276 \pm 0.00586) \times 10^{-5}$ mol/l; curve *2*: $a = (2.18045 \pm 0.00176) \times 10^{-4}$ mol/l, $b = (-0.99257 \pm 0.01554) \times 10^{-4}\ s^{-c}$, $c = 1.41382 \pm 0.00244$, $d = (5.61957 \pm 0.01038) \times 10^{-5}$ mol/l; and curve *3*: $a = (2.41712 \pm 0.00192) \times 10^{-4}$ mol/l, $b = (-1.4135 \pm 0.0195) \times 10^{-4}\ s^{-c}$, $c = 1.45312 \pm 0.00232$, $d = (3.21115 \pm 0.0118) \times 10^{-5}$ mol/l.

The equilibrium constant of the reaction in benzene at 298 K is rather large ($K_{eq}^{298} = 140 \pm 11$ [13]), and, therefore, the reversibility of the reaction at its nonlate stages can be ignored in the absence of the products (H_2QDI and Q). The reaction mechanism (s, –s) includes the following elementary steps [11]:

initiation,

$$\text{(i) TPH} \longrightarrow Ph_2N^{\bullet} \xrightarrow{Ar(OH)_2} Ar(OH)O^{\bullet}$$

chain initiation,

(1, –1) $QDI + Ar(OH)_2 \rightarrow HQDI^{\bullet} + Ar(OH)O^{\bullet}$;

chain propagation,

(2, –2) $QDI + Ar(OH)O^{\bullet} \rightarrow HQDI^{\bullet} + Q$;

(3, –3) $HQDI^{\bullet} + Ar(OH)_2 \rightarrow H_2QDI + Ar(OH)O^{\bullet}$;

chain termination,

(4, –4) $HQDI^{\bullet} + HQDI^{\bullet} \rightarrow H_2QDI + QDI$;

(–1, 1) $HQDI^{\bullet} + Ar(OH)O^{\bullet} \rightarrow QDI + Ar(OH)_2$;

(5, –5) $HQDI^{\bullet} + Ar(OH)O^{\bullet} \rightarrow H_2QDI + Q$;

(6, –6) $Ar(OH)O^{\bullet} + Ar(OH)O^{\bullet} \rightarrow Ar(OH)_2 + Q$.

Scheme.

According to this scheme, the disproportionation of the $Ar(OH)O^{\bullet}$ radical (step 6) is one of the four parallel chain termination reactions.

As can be seen from Fig. 1, the QDI disappearance curves in the absence of an initiator have an autoacceleration period due to the slow establishment of the steady-state radical concentrations in the system [3, 4]. Earlier, we proposed the following empirical formula to fit the S-shaped kinetic profiles of QDI disappearance in chlorobenzene [12]:

$$[QDI] = ae^{bt^c} + d. \quad (1)$$

where t is the reaction time and a, b, c, and d are fitted parameters ($b < 0$, $c > 1$). Figure 1 shows that function (1) provides a good fit to the experimental QDI disappearance curves for benzene as well. The numerical values of a, b, c, and d for some experiments are given in the caption to Fig. 1.

It was suggested to use the QDI disappearance rate (w_{QDI}) at the inflection point of the curve corresponding to Eq. (1) as a kinetic characteristic of the reaction in the steady state [12]. Experience demonstrates that the QDI concentration at the inflection point is usually at least 80% of the initial concentration. Therefore, provided that the equilibrium constant is not very small, w_{QDI} at the reactant concentrations corresponding to the inflection point can be considered an analogue of the initial reaction rate (at $t = 0$).

The coordinates of the inflection point are determined by differentiation of function (1):

$$t_{infl} = e^{\left(\frac{1}{c}\ln\frac{1-c}{bc}\right)}, \quad [QDI]_{infl} = ae^{bt_{infl}^c} + d. \quad (2)$$

The expression for the rate of the reaction can be obtained in the same way:

$$w_{QDI} = -abce^{bt_{infl}^c} t_{infl}^{c-1}. \quad (3)$$

The values of a, b, c, and d are determined by experimental data processing, after which the concentration $[QDI]_{infl}$ is calculated using Eq. (2). The concentrations of the other substances at the inflection point are calculated from their initial concentrations corrected with $[QDI]_{infl}$ and the stoichiometry of the reaction taken into account.

Study of the Reaction between QDI and $Ar(OH)_2$ in the Steady State (Determination of the Rate Constants of Some Elementary Steps)

To determine the disproportionation rate constants of the semiquinone radical $Ar(OH)O^{\bullet}$ (k_6) using the unsteady-state kinetic method presented here, it is necessary to have rate constant data for some other elementary steps. In order to find these constants, one

should use kinetic parameters of the chain reaction between QDI and $Ar(OH)_2$ in the steady state. In this case, the expression for the reaction rate takes the following form [11]:

$$w_{QDI}^2 = \frac{k_2^2 k_3^2 [QDI]^2 [Ar(OH)_2]^2 (k_1 [QDI][Ar(OH)_2] + 0.5 w_i)}{k_4 k_2^2 [QDI]^2 + k_V k_2 k_3 [Ar(OH)_2][QDI] + k_6 k_3^2 [Ar(OH)_2]^2}, \quad (4)$$

where $k_V = k_{-1} + k_5$.

The complicated form of Eq. (4) is due to the fact that the chain reactions of quinone imines with hydroquinones have no rate-determining chain propagation step. For this reason, when setting up an equation for w_{QDI}, we have to take into account all of the four chain termination steps, which involve two types of radicals— $Ar(OH)O^\bullet$ and $HQDI^\bullet$. The great length of the chains in this reaction (10^4–10^5 units [3]) should be taken into account to simplify the situation and to derive Eq. (4). In this case, the following equality is fulfilled with high accuracy:

$$k_2 [QDI][Ar(OH)O^\bullet] = k_3 [HQDI^\bullet][Ar(OH)_2], \quad (5)$$

according to which

$$[HQDI^\bullet] = \frac{k_2 [QDI]}{k_3 [Ar(OH)_2]} [Ar(OH)O^\bullet]. \quad (6)$$

Substituting Eq. (6) into the equation of the steady-state radical formation rate,

$$w_{i\Sigma} = 2k_1 [QDI][Ar(OH)_2] + w_i = 2k_4 [HQDI^\bullet]_{st}^2 + 2(k_{-1} + k_5)[HQDI^\bullet]_{st}[Ar(OH)O^\bullet]_{st} + 2k_6 [Ar(OH)O^\bullet]_{st}^2, \quad (7)$$

we obtain

$$\begin{aligned} &2k_1 [QDI][Ar(OH)_2] + w_i \\ &= 2\left(k_4 \frac{k_2^2 [QDI]^2}{k_3^2 [Ar(OH)_2]^2} + k_V \frac{k_2 [QDI]}{k_3 [Ar(OH)_2]} + k_6 \right) \times [Ar(OH)O^\bullet]_{st}^2 \\ &= 2\left(k_4 + k_V \frac{k_3 [Ar(OH)_2]}{k_2 [QDI]} + k_6 \frac{k_3^2 [Ar(OH)_2]^2}{k_2^2 [QDI]^2} \right) \times [HQDI^\bullet]_{st}^2 \end{aligned} \quad (8)$$

or

$$\begin{aligned} w_{i\Sigma} &= 2k_1 [QDI][Ar(OH)_2] + w_i \\ &= 2k_{Ar(OH)O^\bullet}^{term} [Ar(OH)O^\bullet]_{st}^2 = 2k_{HQDI^\bullet}^{term} [HQDI^\bullet]_{st}^2, \end{aligned} \quad (8a)$$

where $2k_{Ar(OH)O^\bullet}^{term}$ and $2k_{HQDI^\bullet}^{term}$ are the apparent rate constants of quadratic-law chain termination on the $Ar(OH)O^\bullet$ and $HQDI^\bullet$ radicals, which correspond to the factors at $[Ar(OH)O^\bullet]_{st}^2$ and $[HQDI^\bullet]_{st}^2$ in Eq. (8), and $[Ar(OH)O^\bullet]_{st}$ and $[HQDI^\bullet]_{st}$ are the steady-state concentrations of $Ar(OH)O^\bullet$ and $HQDI^\bullet$ radicals in the reaction between QDI and $Ar(OH)_2$. Equation (8a) shows that, for the steady state, the problem is reduced to the equation with one independent variable, $[Ar(OH)O^\bullet]_{st}$ or $[HQDI^\bullet]_{st}$, which makes it possible to obtain the reaction rate equation in the form of equality (4).

At equal concentrations of the reactants, $[QDI]_{infl} = [Ar(OH)_2]_{infl} = c_{infl}$, Eq. (4) is simplified [12]:

$$\begin{aligned} w_{QDI} &= \frac{k_2}{\left(k_4 \frac{k_2^2}{k_3^2} + k_V \frac{k_2}{k_3} + k_6 \right)^{1/2}} c_{infl} \left(k_1 c_{infl}^2 + 0.5 w_i \right)^{1/2} \\ &= \frac{k_2}{(2k_{Ar(OH)O^\bullet}^{term})^{1/2}} c_{infl} w_{i\Sigma}^{1/2}. \end{aligned} \quad (9)$$

Here we take into account that the overall radical formation rate in the system is $w_{i\Sigma} = 2k_1 c_{infl}^2 + w_i$ and the equation

$$k_4 \frac{k_2^2}{k_3^2} + k_V \frac{k_2}{k_3} + k_6 = k_{Ar(OH)O^\bullet}^{term} \quad (10)$$

represents the apparent rate constant of chain termination on semiquinone radicals $Ar(OH)O^\bullet$. In view of this, most experiments were carried out at equal concentrations of the reactants.

Equation (9) can be reduced to the form

$$\begin{aligned} w_{QDI}^2 &= \frac{k_1 k_2^2}{k_{Ar(OH)O^\bullet}^{term}} c_{infl}^4 \\ &+ \frac{k_2^2}{2k_{Ar(OH)O^\bullet}^{term}} c_{infl}^2 w_i = A + B \times c_{infl}^2 w_i, \end{aligned} \quad (11)$$

where c_{infl} stands for the equal concentrations of the reactants QDI and $Ar(OH)_2$ at the inflection point of the QDI disappearance curve calculated using formula (2). As can be seen from Fig. 2, the relationship between w_{QDI}^2 and $c_{infl}^2 w_i$ is indeed linear. From the slope ratio of the straight line in Fig. 2,

$$B = (5.4 \pm 0.1) \times 10^4 \text{ l mol}^{-1} \text{ s}^{-1}$$

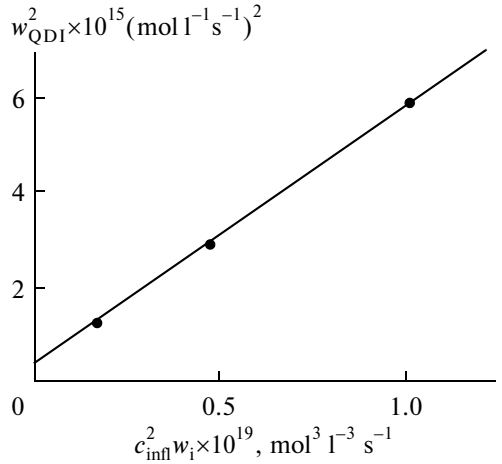


Fig. 2. w_{QDI}^2 versus $c^2 w_i$ for equal reactant concentrations of $[QDI]_0 = [Ar(OH)_2]_0 = 9.0 \times 10^{-5}$ mol/l. The start of the reaction corresponds to the instant the solution of $Ar(OH)_2$ is added to the mixture of QDI and initiator solutions. Benzene as the solvent; $T = 298$ K; argon bubbling.

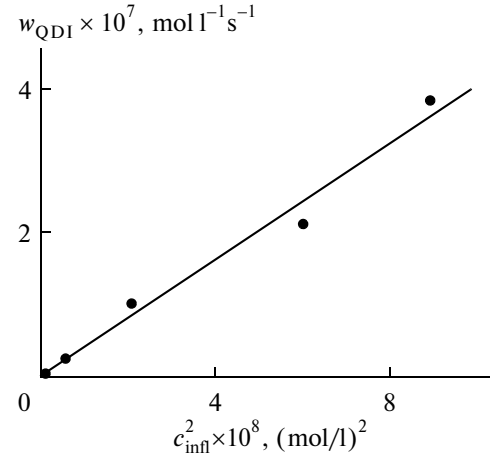


Fig. 3. w_{QDI} versus squared equal concentration of the reactants QDI and $Ar(OH)_2$. Benzene as the solvent; $T =$ 298 K; argon bubbling.

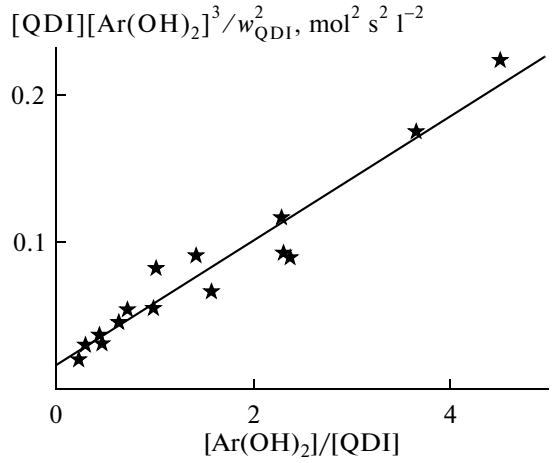


Fig. 4. Representation of the data obtained in the absence of an initiator in the coordinates of Eq. (16). Benzene as the solvent; $T = 298$ K; argon bubbling.

we calculated the parameter

$$k_2/(k_{Ar(OH)O\bullet}^{term})^{1/2} = 332.4 \pm 6.5 \text{ (l mol}^{-1} \text{ s}^{-1})^{1/2}. \quad (12)$$

According to Eq. (11), in the absence of an initiator,

$$w_{QDI} = \frac{k_1^{1/2} k_2}{(k_{Ar(OH)O\bullet}^{term})^{1/2}} c_{infl}^2, \quad (13)$$

that is, the reaction rate w_{QDI} is proportional to the squared concentration c_{infl}^2. Figure 3 shows that this relationship is indeed observed.

From the slope of the straight line in Fig. 3 we find that

$$\frac{k_1^{1/2} k_2}{(k_{Ar(OH)O\bullet}^{term})^{1/2}} = 4.0 \pm 0.35 \text{ l mol}^{-1} \text{ s}^{-1}. \quad (14)$$

The value of k_1 obtained from Eqs. (12) and (14),

$$k_1 = (1.4 \pm 0.3) \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1} \quad (15)$$

does not differ significantly from the value determined for the reaction in chlorobenzene, $k_1 = (9.7 \pm 2.6) \times 10^{-5}$ l mol^{-1} s^{-1} [12].

Earlier we used the results of experiments carried out both in the presence and in the absence of an initiator to determine the chain propagation rate constants k_2 and k_3 [3]. However, a kinetic study of the reaction between QDI and $Ar(OH)_2$ in chlorobenzene [12] showed that only the results obtained in the absence of an initiator should be used for correct determination of k_2 and k_3 for this particular reaction. This fact was taken into account in the present work when determining k_2 and k_3.

In the absence of an initiator ($w_i = 0$), formula (4) can be transformed into

$$\frac{[QDI]_{infl}[Ar(OH)_2]_{infl}^3}{w_{QDI}^2} = \frac{k_4}{k_1 k_3^2} + \frac{k_V}{k_1 k_2 k_3} \frac{[Ar(OH)_2]_{infl}}{[QDI]_{infl}} + \frac{k_6}{k_1 k_2^2} \left(\frac{[Ar(OH)_2]_{infl}}{[QDI]_{infl}} \right)^2. \quad (16)$$

The plot of $[QDI]_{infl}[Ar(OH)_2]_{infl}^3/w_{QDI}^2$ versus $[Ar(OH)_2]_{infl}/[QDI]_{infl}$ is shown in Fig. 4. It can be seen that all points lie on one straight line within the experimental accuracy. Therefore, the last term on the right-hand side of Eq. (16) can be neglected because of its smallness. We measured the ordinate intercepts slopes of the straight lines in shown Fig. 4 and obtained the following values of parameters (mol s l^{-1})^2:

$$\frac{k_4}{k_1 k_3^2} = (1.7 \pm 0.6) \times 10^{-2} \quad \text{and} \quad \frac{k_V}{k_1 k_2 k_3} = (4.20 \pm 0.03) \times 10^{-2}. \quad (17)$$

The following value of $k_2 k_3$ can be obtained from the slope ratio of the straight line in Fig. 4 by accepting

$k_V = 3 \times 10^8$ l mol^{-1} s^{-1} [3, 12] and taking into account that $k_1 = (1.4 \pm 0.25) \times 10^{-4}$ l mol^{-1} s^{-1} (see above):

$$k_2 k_3 = (5.0 \pm 0.9) \times 10^{13} \text{ (l mol}^{-1}\text{ s}^{-1})^2. \quad (18)$$

Using $k_4 = (8 \pm 2) \times 10^8$ l mol^{-1} s^{-1} [14] and the ordinate intercept for the line plotted in Fig. 4 (see Eq. (17)), we obtain

$$k_3 = (1.8 \pm 0.5) \times 10^7 \text{ l mol}^{-1}\text{ s}^{-1}. \quad (19)$$

Then, according to Eq. (18),

$$k_2 = (2.7 \pm 0.8) \times 10^6 \text{ l mol}^{-1}\text{ s}^{-1}, \quad (20)$$

and we find from Eq. (12) that

$$k^{\text{term}}_{\text{Ar(OH)O}^\bullet} = (6.7 \pm 1.9) \times 10^7 \text{ l mol}^{-1}\text{ s}^{-1}. \quad (21)$$

The earlier found rate constants of these elementary steps of the reaction of QDI with $Ar(OH)_2$ in chlorobenzene [12] are presented for comparison: $k_2 = (2.0 \pm 0.2) \times 10^6$, $k_3 = (5.5 \pm 2) \times 10^7$, and $k^{\text{term}}_{\text{Ar(OH)O}^\bullet} = (1.6 \pm 0.1) \times 10^7$ l mol^{-1} s^{-1}. Clearly, the numerical values of the constants are fairly similar for these solvents.

Determination of Rate Constant k_6 from Unsteady-State Kinetic Data for the Initiated Chain Reaction between QDI and Ar(OH)$_2$

It can be seen from Fig. 5 that the initiated reaction between QDI and $Ar(OH)_2$ at the early stages proceeds substantially more rapidly that it might be expected from the QDI disappearance kinetics at later stages. Within the first 20 ± 3 s after the addition of the second reactant ($Ar(OH)_2$ or QDI), i.e., before the beginning of QDI disappearance measurements, the QDI concentration decreases by 10–15%, depending on the TPH concentration ("drawdown" of the QDI concentration), after which the QDI disappearance rate decreases considerably. This observation provides a basis for our method of k_6 determination from the dependence of the decrease in the QDI concentration within the same short time (~20 s) on the initiation rate in a series of experiments at constant QDI and $Ar(OH)_2$ concentrations (i.e., the dependence of the QDI concentration 20 s after the run is started, designated $[QDI]_{20}$, on w_i (see Fig. 5)).

The "drawdown" effect is due to the reaction occurring unsteadily for some time from its start [4]. In our experiments, the reaction was initiated in two ways: (1) addition of $Ar(OH)_2$ to a mixture of QDI and initiator solutions (2) the addition of QDI to a mixture of $Ar(OH)_2$ and initiator solutions. These orders of mixing the reactants and initiator are used in the two different variants of the method developed by us for the determination of k_6.

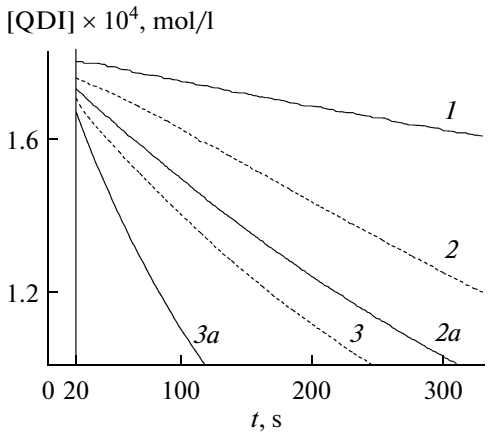


Fig. 5. Experimental QDI disappearance curves for the chain reaction between QDI and $Ar(OH)_2$ in the presence of the initiator at the initiation rate $w_i \times 10^{11} = (1)$ 0, (*2*, *2a*) 1.8, and (*3*, *3a*) 8.8 mol l^{-1} s^{-1}. In all experiments, $[QDI]_0 = [Ar(OH)_2]_0 = 1.8 \times 10^{-4}$ mol/l, the solvent was benzene, $T = 298$ K, and argon bubbling was performed. The order of mixing the reactants: (*2*, *3*) $Ar(OH)_2$ is added to the solution of QDI and initiator; (*2a*, *3a*) QDI is added to the solution of $Ar(OH)_2$ and initiator.

The order of mixing the reactants and initiator affects both the initial decrease in the QDI concentration ("drawdown") and the overall reaction kinetics (Fig. 5). Indeed, one might expect that curve *2* would coincide with curve *2a* and curve *3* would coincide with curve *3a*, but this is not the case.

First variant of the method. In this variant, $Ar(OH)_2$ is added to a solution of QDI with the initiator. The diphenylaminyl radical $Ph_2N^\bullet$ resulting the decomposition of TPH does not react with QDI, and, hence, the steady-state concentration $[Ph_2N^\bullet]_0$ in the solution of TPH and QDI at a given initiation rate w_i is determined only by the recombination rate constant $k_{Ph_2N^\bullet} = 1.8 \times 10^7$ l mol^{-1} s^{-1} [15–18] (Fig. 6). Upon the addition of $Ar(OH)_2$, the $Ph_2N^\bullet$ radicals are rapidly (within ~10^{-4} s at $[Ar(OH)_2]_0 \approx 10^{-4}$ mol/l, because $k \approx 10^8$ l mol^{-1} s^{-1} [19]) replaced by the equivalent concentration of $Ar(OH)O^\bullet$ radicals and the latter are immediately involved in the chain reaction between QDI and $Ar(OH)_2$ as one of the chain carrier radicals:

$$[Ar(OH)O^\bullet]_0 = [Ph_2N^\bullet]_0 = \{w_i/(2k_{Ph_2N^\bullet})\}^{1/2}. \quad (22)$$

If the radical concentration $[Ar(OH)O^\bullet]_0$ before the reaction start exceeds the steady-state radical concentration $[Ar(OH)O^\bullet]_{st}$ during the reaction between QDI and $Ar(OH)_2$, the effect of fast disappearance of the initial reactants ("drawdown" of their concentra-

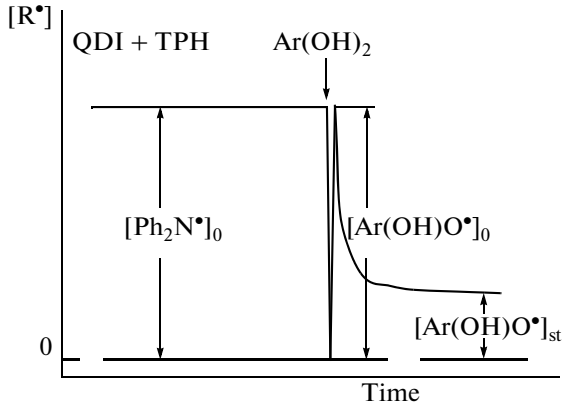


Fig. 6. Change in the nature and concentration of the radicals in the first variant of k_6 determination. The combined QDI + TPH solution contains $Ph_2N^•$ radicals at the concentration $[Ph_2N^•]_0 = \{k_i[TPH]/(2k_{Ph_2N^•})\}^{1/2}$, and the value of $k_{Ph_2N^•}$ is known. The reaction starts at the moment of addition of $Ar(OH)_2$ to the solution of QDI and TPH (indicated with an arrow). The $Ph_2N^•$ radicals are rapidly replaced by an equivalent number of $Ar(OH)O^•$ radicals, after which the initiated chain reaction of QDI with $Ar(OH)_2$ occurs in the presence of the "initial admixture" of the semiquinone radical at the concentration $[Ar(OH)O^•]_0 = [Ph_2N^•]_0 = \{k_i[TPH]/(2k_{Ph_2N^•})\}^{1/2}$.

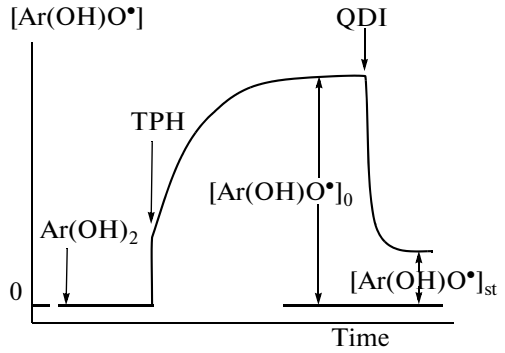


Fig. 7. Change in the concentration of semiquinone radicals in the second variant of the method. The $Ar(OH)_2$ + TPH solution was prepared before the reaction. The initial TPH solution contains $Ph_2N^•$ radicals at the equilibrium concentration $[Ph_2N^•]_{eq} = \{k_i[TPH]/(2k_{Ph_2N^•})\}^{1/2}$. Upon the addition of TPH to the solution of $Ar(OH)_2$ (indicated with an arrow), the $Ph_2N^•$ radicals are rapidly replaced by $Ar(OH)O^•$ radicals in an equivalent amount, but at a concentration lower than $[Ph_2N^•]_{eq}$ because of the dilution of the TPH solution. Thereafter, the concentration of $Ar(OH)O^•$ radicals increases (or decreases) to $[Ar(OH)O^•]_0 = \{k_i[TPH]/(2k_6)\}^{1/2}$, where k_6 is the sought rate constant. Upon the addition of the QDI solution (indicated with an arrow), the initiated chain reaction between QDI and $Ar(OH)_2$ occurs in the presence of the "initial admixture" of the semiquinone radical at the concentration $[Ar(OH)O^•]_0 = \{k_i[TPH]/(2k_6)\}^{1/2}$.

tions) can be observed at the early stages, which is used in the determination of k_6. As mentioned above (see Eqs. (8) and (8a)), at a given rate w_i the value of $[Ar(OH)O^•]_{st}$ is determined by the apparent rate constant of chain termination on $Ar(OH)O^•$ radicals ($k_{Ar(OH)O}$) during the reaction:

$$[Ar(OH)O^•]_{st} = \{w_{i\Sigma}/(2k_{Ar(OH)O})\}^{1/2}, \qquad (8b)$$

where $w_{i\Sigma} = w_i + 2k_1[QDI][Ar(OH)_2]$. It was also shown above that the expression for $k_{Ar(OH)O}$ is substantially simpler for equal reactant concentrations, $[QDI]_0 = [Ar(OH)_2]_0$, and can be written as Eq. (10) with $k_4 = 8 \times 10^8$ l mol^{-1} s^{-1} [14] and $k_V = k_{-1} + k_5 = 3 \times 10^8$ l mol^{-1} s^{-1} [3, 12]. It is clear from Fig. 6 that the first variant of the method is usable provided that $k_{Ph_2N^•} < k_{Ar(OH)O}$.

The second variant of the method. In the second variant, QDI is added to a solution of $Ar(OH)_2$ and the initiator. The solution of $Ar(OH)_2$ with the initiator TPH is stored for time t in order to accumulate semiquinone radicals $Ar(OH)O^•$ at the concentration

$$[Ar(OH)O^•]_0 = (w_i/(2k_6))^{1/2} \qquad (23)$$

via the decomposition of the initiator followed by the reaction of $Ph_2N^•$ with $Ar(OH)_2$. The addition of the QDI solution initiates the reaction between QDI and $Ar(OH)_2$ proceeding in the presence of the initial semiquinone radical concentration $[Ar(OH)O^•]_0$ (see Fig. 7).

In both variants, the reaction is monitored as the disappearance of QDI, its concentration being $[QDI]_t$ at the instant the monitoring is begun (20 s after the start of the reaction, which is initiated by adding $Ar(OH)_2$ in the first variant and QDI in the second one). Figure 7 shows that the second variant of the method is usable provided that $k_6 < k_{Ar(OH)O}$.

It was shown above that, when describing the steady-state kinetics of the reaction of QDI with $Ar(OH)_2$, all chain termination reactions can be approximated by a radical disproportionation reaction on radicals of one type with a quite definite apparent rate constant, for example, $k^{term}_{Ar(OH)O}$ (see Eqs. (8) and (8a)). It is important that this simplification is also applicable to the stage of system relaxation into the steady state, when the concentration of semiquinone radicals decreases from $[Ar(OH)O^•]_0$ to the quasi-steady-state value $[Ar(OH)O^•]_{st}$. This conclusion can be drawn by taking into account that the rates of steps (2) and (3) in the above scheme are several orders of magnitude higher than the rates of the other steps. At reactant concentrations of $[QDI]_0 \approx [Ar(OH)_2]_0 \approx 1 \times 10^{-4}$ mol/l, the characteristic times of steps (2) and (3) are very short: $\tau_2 =$

$(k_2[\mathrm{QDI}])^{-1} \approx 10^{-3}$ and $\tau_3 = (k_3[\mathrm{Ar(OH)_2}])^{-1} \approx 10^{-4}$ s. Taking the aforesaid into account, we conclude that the value of $k_{\mathrm{Ar(OH)O}}$ in the experiments with equal concentrations $[\mathrm{QDI}]_0 = [\mathrm{Ar(OH)_2}]_0$ can be considered invariable both during the relaxation of the system to the steady state and after the steady state is reached. The validity of Eq. (6) was checked by computer simulation using the above values of k. The results of this simulation demonstrated that, at the reactant and initiator concentrations used in the work, Eq. (6) is obeyed with high accuracy already after ~10^{-3} s, i.e., almost from the beginning of the reaction.

Thus, the Ar(OH)O$^\bullet$ disappearance kinetics, can be described by the equation

$$\frac{\mathrm{d}[\mathrm{Ar(OH)O^\bullet}]}{\mathrm{d}t} = w_{i\Sigma} - 2k_{\mathrm{Ar(OH)O}}[\mathrm{Ar(OH)O^\bullet}]^2, \quad (24)$$

where $w_{i\Sigma} = w_i + 2k_1[\mathrm{QDI}][\mathrm{Ar(OH)_2}]$ and $k_{\mathrm{Ar(OH)O}}$ is the apparent rate constant of the quadratic-law decay of semiquinone radicals, which is constant in this experiment (see Eq. (10)). Integrating Eq. (24) subject to the initial condition that $[\mathrm{Ar(OH)O^\bullet}] = [\mathrm{Ar(OH)O^\bullet}]_0$ at $t = 0$, we obtain an expression describing the time variation of the semiquinone radical concentration [Ar(OH)O$^\bullet$]. The rate of QDI disappearance via the chain reaction is equal to the rate of step (2) in the above scheme of the reaction:

$$-\frac{\mathrm{d}[\mathrm{QDI}]}{\mathrm{d}t} = k_2[\mathrm{QDI}][\mathrm{Ar(OH)O^\bullet}]. \quad (25)$$

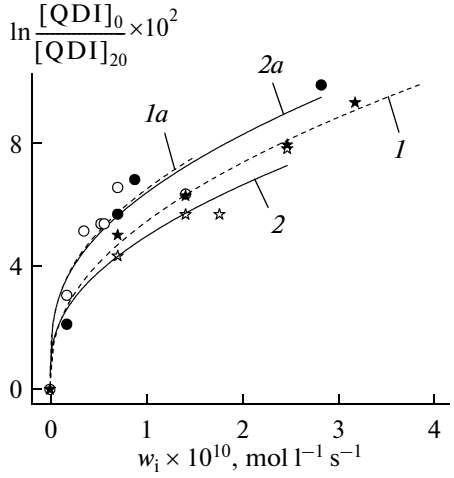


Fig. 8. $\ln([\mathrm{QDI}]_0/[\mathrm{QDI}]_t)$ versus w_i in the series of experiments at equal reactant concentrations: (*1*, *1a*) $[\mathrm{QDI}]_0 = [\mathrm{Ar(OH)_2}]_0 = 9 \times 10^{-5}$ mol/l and (*2*, *2a*) $[\mathrm{QDI}]_0 = [\mathrm{Ar(OH)_2}]_0 = 1.8 \times 10^{-4}$ mol/l. Benzene as solvent; $T =$ 298 K; argon bubbling. The points reprtesent experimental data, and the lines are fits of experimental data to formula (4). The order of reactant mixing: (*1*, *2*) $\mathrm{Ar(OH)_2}$ is added to the QDI + initiator solution (first variant); (*1a*, *2a*) QDI is added to the $\mathrm{Ar(OH)_2}$ + initiator solution (second variant).

Substituting the expression for [Ar(OH)O$^\bullet$] obtained by the integration of Eq. (24) into Eq. (25) and integrating Eq. (25) subject to the initial condition that $[\mathrm{QDI}] = [\mathrm{QDI}]_0$ at $t = 0$, we arrive at the equation

$$\ln\frac{[\mathrm{QDI}]_0}{[\mathrm{QDI}]_t} = -k_2[\mathrm{Ar(OH)O^\bullet}]_{st}t + \frac{k_2}{2k_{\mathrm{Ar(OH)O}}}\ln\frac{([\mathrm{Ar(OH)O^\bullet}]_0 + [\mathrm{Ar(OH)O^\bullet}]_{st})e^{4k_{\mathrm{Ar(OH)O}}[\mathrm{Ar(OH)O^\bullet}]_{st}t} - ([\mathrm{Ar(OH)O^\bullet}]_0 - [\mathrm{Ar(OH)O^\bullet}]_{st})}{2[\mathrm{Ar(OH)O^\bullet}]_{st}}. \quad (26)$$

Here, $[\mathrm{QDI}]_0$ is the analytically prescribed initial quinone diimine concentration and $[\mathrm{QDI}]_t$ is the experimentally measured quinone diimine concentration at the beginning of QDI disappearance measurements ($t = 20$ s). The $[\mathrm{Ar(OH)O^\bullet}]_{st}$ and $k_{\mathrm{Ar(OH)O}}$ values have the meaning indicated above (see Eqs. (8b) and (10), respectively). Equation (22) should be used for calculating $[\mathrm{Ar(OH)_2}]_0$ in the first variant of the method; Eq. (23), in the second variant. Clearly, the right-hand side of equality (26) depends only on w_i and k_6 since the other rate constants necessary for calculation were determined by steady-state experiments (see above). Thus, the numerical values of k_6 can be derived by iterative methods from the dependence of $\ln([\mathrm{QDI}]_0/[\mathrm{QDI}]_t)$ on w_i in a series of experiments at equal concentrations of QDI and $\mathrm{Ar(OH)_2}$.

The results of experimental data processing are presented in Fig. 8. The numerical values of k_6 obtained in this work are given in the table.

The k_6 values found by the two variants of the method are in agreement within the experimental error and almost coincide with the value obtained earlier for the reaction in chlorobenzene, $k_6 = (5.8–7.1) \times$

Table

Variant of the method	Concentration $\times 10^5$, mol/l	$k_6 \times 10^{-6}$, l mol^{-1} s^{-1}
1	$[QDI]_0 = [Ar(OH)_2]_0 = 9.0$	5.1 ± 2.8
	$[QDI]_0 = [Ar(OH)_2]_0 = 18.0$	9.4 ± 4.2
	Average	7.3 ± 3.7
2	$[QDI]_0 = [Ar(OH)_2]_0 = 9.0$	4.4 ± 2.0
	$[QDI]_0 = [Ar(OH)_2]_0 = 18.0$	5.5 ± 2.5
	Average	5.0 ± 2.2

10^6 l mol^{-1} s^{-1} [4]. It was noted above that these k_6 values differ considerably from the value $k_6 \approx 10^8$ l mol^{-1} s^{-1} found for the reactions of other semiquinone radicals [5]. The difference is likely due to the fact that most of the earlier reported k_6 values [5] were obtained by pulse methods in polar solvents (because of the very low solubility of hydroquinones in other solvents). We studied the disproportionation reaction in nonpolar and weakly polar solvents using unsteady-state kinetic data for the chain reactions of quinone imines with hydroquinones. A standard spectrophotometer was used in the measurements, and the measurement time was tens of seconds.

Several ways of using unsteady-state kinetic data to determine the chain termination rate constants in chain reactions were described: intermittent illumination [20–22] and photochemical pre- and aftereffect [23, 24] techniques and chemiluminescence-based photochemical and oxygen aftereffect methods [25]. Both variants of our k_6 determination method are similar to the earlier developed methods, but differ from them at the same time. For instance, since all of the above methods were developed for chain reactions with quadratic-law chain termination, calculations in all of them are performed using an equation similar to Eq. (24) with a constant chain termination rate constant. In our method, the degree of disappearance of one of the reactants (QDI) is used in the determination of k_6. This fact makes this method similar to the intermittent illumination and photochemical aftereffect techniques,[1] but not to the chemiluminescence methods, in which the measured glow intensity is proportional to the squared concentration of intermediates (peroxyl radicals). In our method, the initiation rate remains unchanged during the experiment. In this respect, the method resembles the chemiluminescence-based oxygen aftereffect method.[2] Note that our method enabled us to determine, for the first time, not only the apparent chain termination rate constant for the reaction between QDI and $Ar(OH)_2$ ($k^{term}_{Ar(OH)O^\bullet}$), but also the rate constant k_6 of Ar(OH)O$^\bullet$ disproportionation, which is one of the four parallel chain termination steps in this reaction.

Thus, we suggest two variants of the method based on the unsteady-state kinetics of the initiated reaction between QDI and $Ar(OH)_2$ for determining the disproportionation rate constant of the semiquinone radical Ar(OH)O$^\bullet$. The nonstationary regime of the reaction is caused by the presence of semiquinone radicals accumulated before the start of the reaction in the system. Their concentration $[Ar(OH)O^\bullet]_0$ exceeds the steady-state concentration $[Ar(OH)O^\bullet]_{st}$ during the chain reaction of QDI with $Ar(OH)_2$. At the start of the reaction, the reaction mixture should be considered as a four-component system consisting of the reactants QDI and $Ar(OH)_2$, initiator TPH, and an "admixture" in the form of semiquinone radicals Ar(OH)O$^\bullet$. The variants of the method differ in the way of accumulation and concentration of the Ar(OH)O$^\bullet$ "admixture." In the first variant, the reaction is initiated by the addition of $Ar(OH)_2$ to a solution of QDI and initiator. In this case, the constant $k_{Ph_2N^\bullet}$ is known and the Ar(OH)O$^\bullet$ concentration is calculated via formula (22). In the second variant, the reaction is initiated by the addition of QDI to a solution of $Ar(OH)_2$ and initiator. The Ar(OH)O$^\bullet$ concentration is calculated using formula (23) in which the constant k_6 should be determined.

[1] The amount of the resulting reaction product is also used in these methods to determine k.

[2] In the other methods, the initiation rate changes sharply, depending on illumination.

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