

# Reversible Chain Reaction between *N,N'*-Diphenyl-1,4-Benzoquinonediimine and 2,5-Dichlorohydroquinone: Kinetics, Mechanism, and the Rate Constants of Elementary Steps

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**Abstract**—The kinetics of the reversible chain reaction between *N,N'*-diphenyl-1,4-benzoquinonediimine and 2,5-dichlorohydroquinone was studied in chlorobenzene at 298 and 343 K. Experiments in the presence of an initiator proved that the reaction proceeds via a chain mechanism with a chain length of  $\sim 10^4$  to  $10^5$  units, depending on the reactant and initiator concentrations and temperature. The reaction rate first increases and then decreases with increasing concentrations of the reaction products (*N,N'*-diphenyl-1,4-phenylenediamine and 2,5-dichloroquinone) due to the pronounced reversibility of the chain termination and propagation steps involving the reaction products. The reaction orders with respect to the components were determined. The rate constants and activation energies of most of the elementary steps of the forward and backward chain reactions were determined or reliably estimated. Induction periods were observed for the first time in the reversible chain reactions in the quinoneimine + hydroquinone systems. The induction periods are due to the long time required for the establishment of the steady-state radical concentrations in the system.

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## INTRODUCTION

It was demonstrated in 1993 by the example of the reaction between *N*-phenyl-1,4-benzoquinone monoimine  $O=C_6H_4=N-C_6H_5$  and 2,5-di-*tert*-butylhydroquinone that the reactions between quinoneimines and hydroquinones proceed via a chain mechanism [1]. The pronounced reversibility of two elementary steps of the chain mechanism of this reaction (large rate constants of the backward reactions) was observed in the presence of one of the products, namely, 4-hydroxydiphenylamine [2]. Based on these data, we suggested that, in the general case, the reactions between quinoneimines and hydroquinones should be considered as reversible liquid-phase chain reactions [3] in which the equilibrium is reached through a chain route from both the starting reactants and the products. This hypothesis has recently been confirmed experimentally for the reaction between *N*-phenyl-1,4-benzoquinone monoimine and 2,5-dichlorohydroquinone [4–6].

The reactions between quinoneimines and hydroquinone are of theoretical and practical interest. Quinoneimines are nitrogen-containing analogues of quinones, and, therefore, the reactions of quinoneimines with hydroquinones are models of the reactions between quinones and hydroquinones and, more generally, of H atom abstraction from valence-saturated compounds by quinones and quinoneimines. Quinones are widely used as inhibitors of radical polymerization

[7–9]. Quinones and quinoneimines form from phenolic and aromatic amine antioxidants under inhibited oxidation conditions and substantially affect the total efficiency of these antioxidants [9–12]. The mechanism of the reactions between quinones and hydroquinones is of obvious interest to biochemistry because some quinones (ubiquinones, vitamin K group) are strong lipid-soluble bioantioxidants [13] and H atom abstraction reactions play an important role in their protective action [12].

The kinetics of three chain reactions in the quinoneimine + hydroquinone systems has been studied to date, namely, the reactions of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-di-*tert*-butyl- [1, 3], 2,5-dimethyl- [14], and 2,5-dichlorohydroquinones [5, 6]. In the present work, we report the kinetics of the reversible chain reaction between *N,N'*-diphenyl-1,4-benzoquinonediimine  $C_6H_5-N=C_6H_4=N-C_6H_5$  (QDI) and 2,5-dichlorohydroquinone 4-HO-2,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>2</sub>OH (Ar(OH)<sub>2</sub>) in chlorobenzene. This reaction is characterized by very long chains of  $\sim 10^5$  units. Another important feature of the reaction is a well-defined induction period, which is observed for the first time for chain reactions between a quinoneimine and a hydroquinone.

## EXPERIMENTAL

The synthesis and purification of the reactants (QDI,  $\text{Ar(OH)}_2$ , *N,N'*-diphenyl-1,4-phenylenediamine ( $\text{H}_2\text{QDI}$ ), 2,5-dichloroquinone (Q), tetraphenylhydrazine (TPH) initiator) and chlorobenzene as the solvent were described earlier [15, 16]. Kinetics was studied at  $T = 298 \pm 0.1$  and  $343 \pm 0.5$  K in a temperature-controlled quartz bubbled cell built in a Specord UV VIS spectrophotometer (cell volume of 8.5 ml, optical path length of  $l = 2.0$  cm, argon bubbling). The spectrophotometer was coupled to a computer. Absorbance was measured at a certain absorption band of QDI, specifically,  $\nu_{22260}$ , 20000, or 19000  $\text{cm}^{-1}$ , depending on the initial QDI concentration, at 1–10 s intervals. The reaction product 2,5-dichloroquinone also absorbs, though weakly, in this region, but its absorption was neglected because of its small molar extinction coefficient ( $\epsilon_{\text{Q}}^{22260} \sim 20 \text{ l mol}^{-1} \text{ cm}^{-1}$ ,  $\epsilon_{\text{QDI}}^{22260} \sim 7 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ ). The true concentrations of the reactants at 343 K were calculated with allowance made for the thermal expansion of chlorobenzene ( $1 \times 10^{-3} \text{ deg}^{-1}$ ), and experimental  $\epsilon_{\text{QDI}}$  values for 343 K [16] were used in the calculation of the QDI concentration.

The reaction kinetics was studied in terms of the initial disappearance rates of QDI ( $w_{\text{QDI}}$ ). In the general case, the QDI disappearance curves indicated an induction period (especially at  $T = 298$  K), whose duration increased with decreasing reactant concentrations to become  $\sim 1.5$ – $4.5$  min at the lowest QDI and  $\text{Ar(OH)}_2$  concentrations ( $\sim (5\text{--}9) \times 10^{-5} \text{ mol/l}$ ). In the presence of the TPH initiator or Q, the QDI concentration measured immediately after the cell compartment was closed (start of measurements) was lower than the analytically predetermined concentration, and it decreased with an increase in the TPH or Q concentration. For this reason, numerical  $w_{\text{QDI}}$  values were determined by fitting the QDI disappearance curves from the end of the induction period to the instant of 50–75% QDI conversion to the empirical equation

$$[\text{QDI}] = ae^{-b(t-\tau)} + c,$$

where  $a$ ,  $b$ ,  $\tau$ , and  $c$  are the parameters fitted by iterations. Accordingly,

$$w_{\text{QDI}} = ab \times \exp(-\ln(a/([\text{QDI}]_0 - c))).$$

## RESULTS AND DISCUSSION

The reaction between QDI and  $\text{Ar(OH)}_2$  involves the reduction of QDI to *N,N'*-diphenyl-1,4-phenylenediamine ( $\text{H}_2\text{QDI}$ ) due to the oxidation of  $\text{Ar(OH)}_2$  to 2,5-

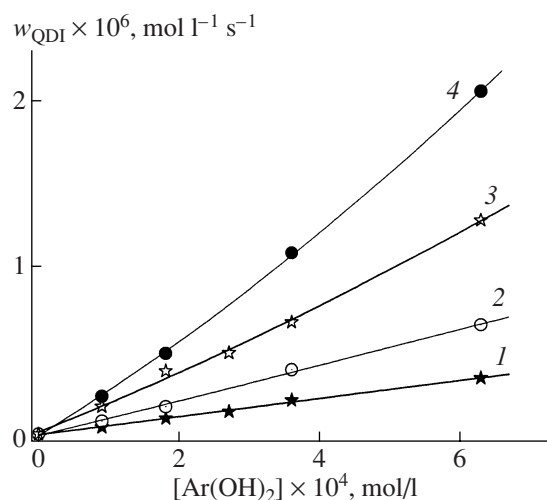
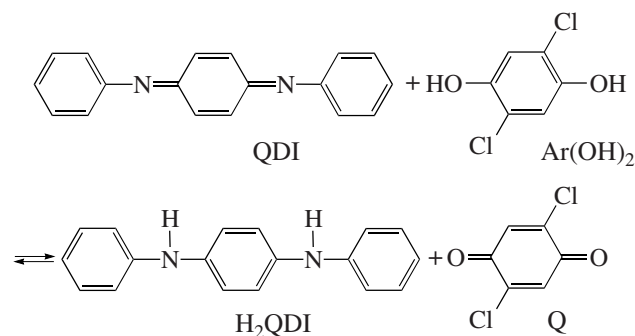


Fig. 1. Initial rate of the reaction as a function of the  $\text{Ar(OH)}_2$  concentration in chlorobenzene at 298 K:  $[\text{QDI}] = (1) 0.90 \times 10^4$ , (2)  $1.80 \times 10^4$ , (3)  $3.60 \times 10^4$ , and (4)  $6.30 \times 10^4$  mol/l.

dichlorohydroquinone (Q):



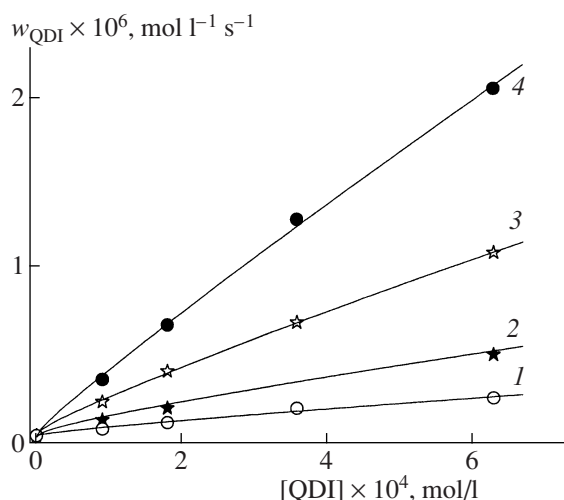
The reaction is complete when the deficient reactant is almost entirely consumed. The temperature dependence of  $K_{\text{eq}}$  in chlorobenzene between 298 and 364 K was studied earlier [16]:  $\Delta S = -0.2 \pm 0.05 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\Delta H = -11.3 \pm 0.1 \text{ kJ/mol}$ ; accordingly, the  $K_{\text{eq}}$  values at 298 and 343 K are

$$K_{\text{eq}}^{298} = 92 \pm 13, \quad K_{\text{eq}}^{343} = 50 \pm 7.$$

Similar results ( $K_{\text{eq}}^{298} = 91.9$ ,  $K_{\text{eq}}^{343} = 54.8$ ) were obtained in the present study (single experiments).

The dependence of  $w_{\text{QDI}}$  on the concentration of one of the components at a constant concentration of the other was studied to determine the reaction orders with respect to the components. The results obtained at  $T = 298$  K are presented in Figs. 1 and 2. Representing these data in the  $\ln w_{\text{QDI}} - \ln [\text{Ar(OH)}_2]_0$  coordinates (at  $[\text{QDI}]_0 = \text{const}$ ) and  $\ln w_{\text{QDI}} - \ln [\text{QDI}]_0$  (at  $[\text{Ar(OH)}_2]_0 = \text{const}$ ) gave the following results:

$T, \text{ K}$	298	343
$n_{\text{Ar(OH)}_2}$	$1.09 \pm 0.02$	$1.11 \pm 0.05$
$n_{\text{QDI}}$	$0.92 \pm 0.02$	$0.86 \pm 0.03$



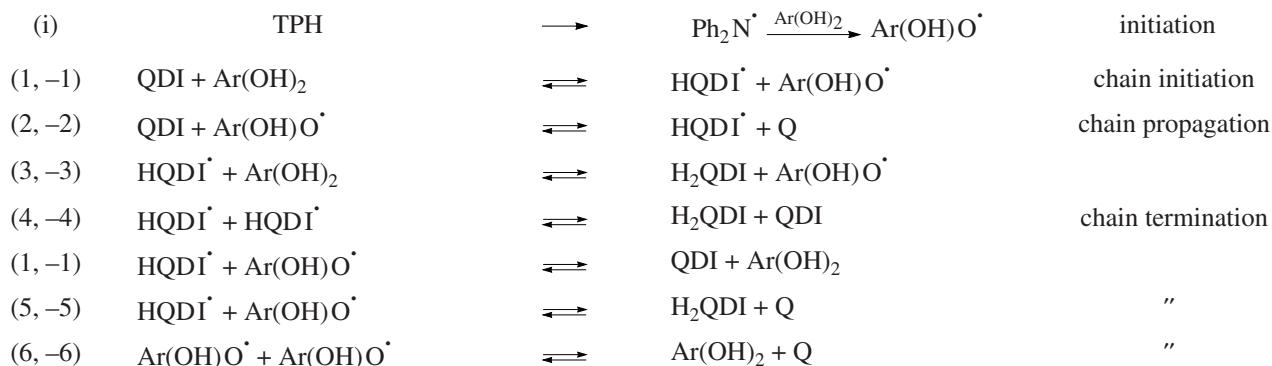
**Fig. 2.** Initial rate of the reaction as a function of the QDI concentration in chlorobenzene at 298 K:  $[\text{Ar}(\text{OH})_2] = (1) 0.90 \times 10^4$ , (2)  $1.80 \times 10^4$ , (3)  $3.60 \times 10^4$ , and (4)  $6.30 \times 10^4$  mol/l.

The fractional orders indicate a complicated mechanism of the reaction.

To prove that the reaction takes place via a chain mechanism, we carried out experiments in the presence of the tetraphenylhydrazine ( $\text{Ph}_2\text{N}-\text{NPh}_2$ ) initiator, which decomposes upon heating to diphenylaminyl ( $\text{Ph}_2\text{N}^\bullet$ ) radicals. The latter abstract an H atom from

$\text{Ar}(\text{OH})_2$  very actively ( $k \sim 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  [17]) to form the hydroxyphenoxyl (semiquinone) radical  $\text{Ar}(\text{OH})\text{O}^\bullet$ . The rate constants of initiation due to TPH decomposition ( $k_i$ ) were calculated using the formula  $k_i = 2e k_{\text{dec}}^{\text{TPH}} = 1.90 k_{\text{dec}}^{\text{TPH}}$ , where  $e = 0.95 \pm 0.015$  is the probability of the radical escaping to the bulk and  $k_{\text{dec}}^{\text{TPH}} (\text{s}^{-1}) = 10^{13.89} \exp(-117500/RT)$  (the energy is in J/mol) [3]. At 298 and 343 K,  $k_i = 3.91 \times 10^{-7}$  and  $1.96 \times 10^{-4} \text{ s}^{-1}$ , respectively. As can be seen from the data in Fig. 3, the reaction rate is much higher in the presence of the initiator and a linear relationship between  $w_{\text{QDI}}^2$  and  $w_i$  is observed. This indicates that the reaction proceeds via a chain mechanism with quadratic-law chain termination. The ordinate intercepts of the straight lines in Fig. 3b are positive, indicating that radical formation in the QDI +  $\text{Ar}(\text{OH})_2$  system in the absence of the initiator is due to intrinsic processes. The chain lengths can be estimated from data presented in Fig. 3. For example, at  $T = 298 \text{ K}$  a  $\sim 10^{-12} \text{ mol l}^{-1} \text{ s}^{-1}$  increase in  $w_i$  causes a  $\sim 5 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$  increase in  $w_{\text{QDI}}$ , whence it follows that the chain length is  $\nu = \Delta w_{\text{QDI}} / \Delta w_i \sim 5 \times 10^4$  units.

The mechanism of the reactions between quinone-imines and hydroquinones includes the following elementary steps [1, 3]:



Here,  $\text{Ar}(\text{OH})\text{O}^\bullet$  and  $\text{HQDI}^\bullet$  are the radicals resulting from hydrogen atom abstraction from 2,5-dichloro-hydroquinone ( $\text{Ar}(\text{OH})_2$ ) and *N,N'*-diphenyl-1,4-phenylenediamine ( $\text{H}_2\text{QDI}$ ).

As was noted above, the reaction between QDI and  $\text{Ar}(\text{OH})_2$  can be considered as irreversible because of the large  $K_{\text{eq}}$  values. Accordingly, to obtain an expression for the reaction rate, one can use the long chain equation, which is satisfied with a high accuracy at  $\nu \sim 10^4$ :

$$w_{\text{QDI}} = k_2[\text{QDI}][\text{Ar}(\text{OH})\text{O}^\bullet] = k_3[\text{HQDI}^\bullet][\text{Ar}(\text{OH})_2]. \quad (1)$$

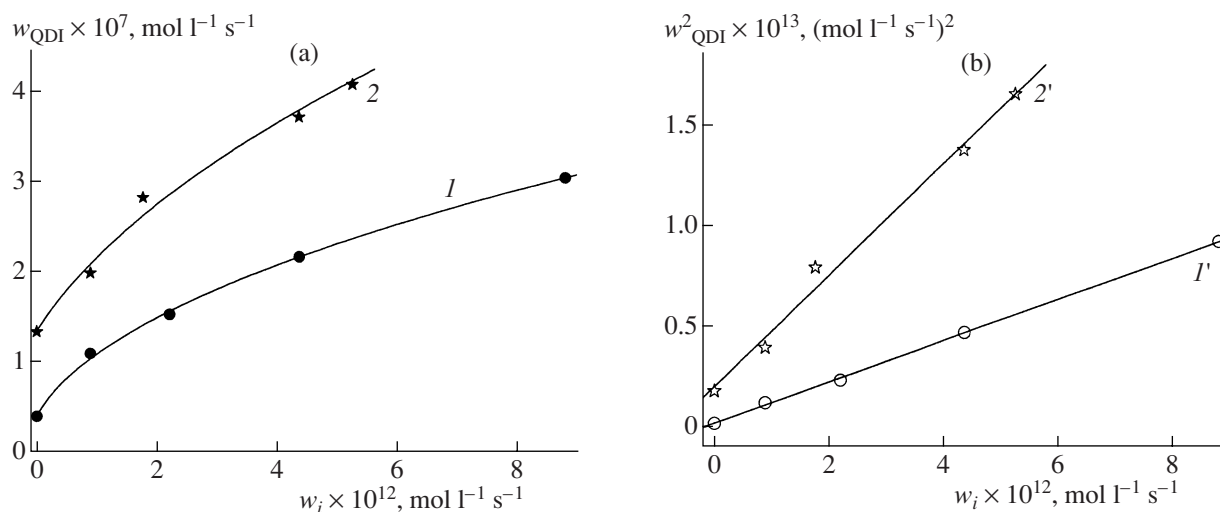
Expressing the  $\text{HQDI}^\bullet$  and  $\text{Ar}(\text{OH})\text{O}^\bullet$  concentrations in terms of  $w_{\text{QDI}}$  from Eq. (1), we obtain

$$[\text{Ar}(\text{OH})\text{O}^\bullet] = \frac{w_{\text{QDI}}}{k_2[\text{QDI}]}, \quad (2)$$

$$[\text{HQDI}^\bullet] = \frac{w_{\text{QDI}}}{k_3[\text{Ar}(\text{OH})_2]}.$$

The substitution of Eq. (2) into the steady-state equation

$$k_1[\text{QDI}][\text{Ar}(\text{OH})_2] + 0.5w_i = k_4[\text{HQDI}^\bullet]^2 + (k_{-1} + k_5)[\text{HQDI}^\bullet][\text{Ar}(\text{OH})\text{O}^\bullet] + k_6[\text{Ar}(\text{OH})\text{O}^\bullet]^2, \quad (3)$$



**Fig. 3.** (a) (1, 2)  $w_{\text{QDI}}$  versus the initiation rate for the reaction between QDI and  $\text{Ar}(\text{OH})_2$ . (b) Linearization of (1') curve 1 and (2') curve 2 as  $w_{\text{QDI}}^2$  versus  $w_i$ .  $[\text{QDI}]_0 = \text{const} = 9.0 \times 10^{-5} \text{ mol/l}$ ;  $[\text{Ar}(\text{OH})_2]_0 = (1, 1') 9.0 \times 10^{-5}$  and  $(2, 2') 1.80 \times 10^{-4} \text{ mol/l}$ .

yields

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

where  $k_v = k_{-1} + k_5$ . At  $w_i = 0$ , Eq. (4) can be rewritten as

$$\frac{[\text{QDI}] [\text{Ar}(\text{OH})_2]^3}{w_{\text{QDI}}^2} = \frac{k_4}{k_1 k_3^2} + \frac{k_v}{k_1 k_2 k_3} \frac{[\text{Ar}(\text{OH})_2]}{[\text{QDI}]} + \frac{k_6}{k_1 k_2^2} \left( \frac{[\text{Ar}(\text{OH})_2]}{[\text{QDI}]} \right)^2. \quad (5)$$

Figure 4 plots  $[\text{QDI}] [\text{Ar}(\text{OH})_2]^3 / w_{\text{QDI}}^2$  versus  $[\text{Ar}(\text{OH})_2] / [\text{QDI}]$  in the absence of the initiator (data for  $T = 298 \text{ K}$ ; see Figs. 1 and 2). At  $T = 298$  and  $343 \text{ K}$ , all points lie in straight lines within the experimental error. This means that the last term on the right-hand side of Eq. (5) can be neglected; i.e., the chain termination stage (VI) can be ignored under the given experimental conditions.

The following parameters were derived from the ordinate intercepts and slopes of the straight lines in Fig. 4:

Parameter	298 K	343 K
$\frac{k_4}{k_1 k_3^2},$ ( $\text{mol s l}^{-1})^2$	$(7.3 \pm 1.4) \times 10^{-3}$	$(5.7 \pm 1.4) \times 10^{-5}$
$\frac{k_v}{k_1 k_2 k_3},$ ( $\text{mol s l}^{-1})^2$	$(2.82 \pm 0.06) \times 10^{-2}$	$(1.53 \pm 0.08) \times 10^{-4}$

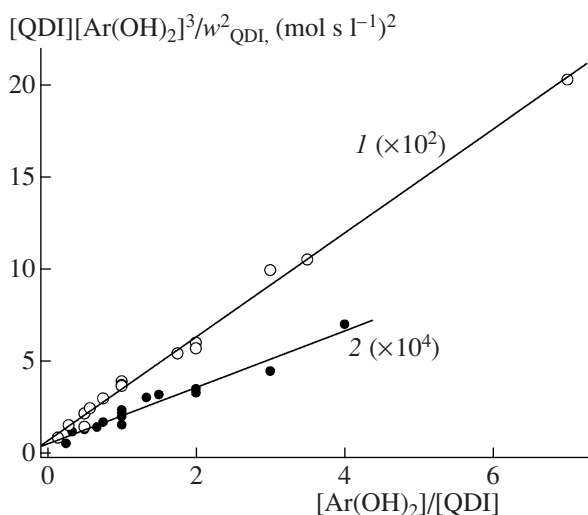
The data obtained in the presence of the initiator were fitted to the equation

$$\frac{[\text{QDI}] + \alpha [\text{Ar}(\text{OH})_2]}{[\text{QDI}]^2 [\text{Ar}(\text{OH})_2]^3} w_{\text{QDI}}^2 = \frac{k_1 k_3^2}{k_4} + \frac{0.5 k_3^2 w_i}{k_4 [\text{QDI}] [\text{Ar}(\text{OH})_2]}, \quad (6)$$

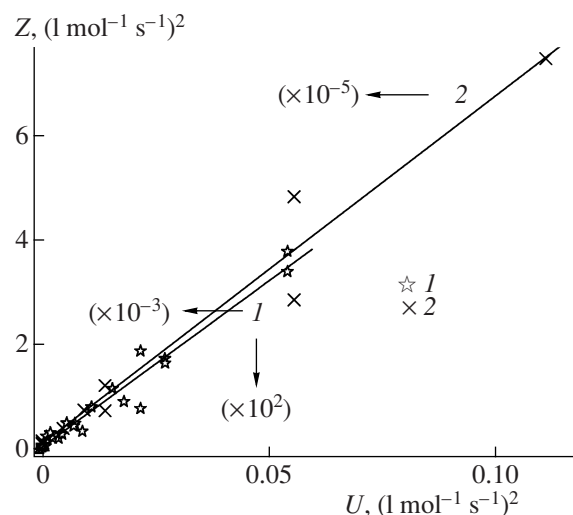
which can be obtained from Eq. (4) by neglecting the contribution from reaction (VI). Here, the parameter  $\alpha = k_3 k_v / (k_2 k_4)$  is introduced. Its numerical values were derived from the kinetic parameters given above:  $\alpha = 3.84 \pm 0.76$  at  $T = 298 \text{ K}$  and  $\alpha = 2.67 \pm 0.67$  at  $T = 343 \text{ K}$ .

Let the left-hand side of Eq. (6) be designated  $Z$  and  $w_i / ([\text{QDI}] [\text{Ar}(\text{OH})_2]) = U$ . Equation (6) will then appear as

$$Z = \frac{k_1 k_3^2}{k_4} + 0.5 \frac{k_3^2}{k_4} U. \quad (6a)$$



**Fig. 4.** Fitting of experimental data in the absence of the initiator to Eq. (5) (chlorobenzene, argon bubbling) at (1) 298 and (2) 343 K.



**Fig. 5.** Fitting of experimental data in the presence of the initiator to Eq. (6a) at (1) 298 K (27 entries) and (2) 343 K (11 entries).

As can be seen from Fig. 5, Eq. (6a) is in good agreement with the experiment. The parameters of the straight lines in Fig. 5 have the following values:

Parameter	298 K	343 K
$\frac{k_1 k_3^2}{k_4}$ , ( $\text{l mol}^{-1} \text{s}^{-1}$ ) <sup>2</sup>	$(1.10 \pm 0.45) \times 10^2$	$(1.78 \pm 0.68) \times 10^4$
$0.5 \frac{k_3^2}{k_4}$ , $\text{l mol}^{-1} \text{s}^{-1}$	$(6.3 \pm 0.25) \times 10^6$	$(6.6 \pm 0.4) \times 10^6$

From these data, we can derive  $k_1$ , but with a rather large error (>40%). To obtain more accurate  $k_1$  data, we simultaneously used the above experimental data for the reaction without the initiator (Eq. (5)) and for the reaction involving the initiator (Eq. (6)). The following  $k_1$  values ( $\text{l mol}^{-1} \text{s}^{-1}$ ) were thus obtained:

$$k_1(298 \text{ K}) = (1.1 \pm 0.25) \times 10^{-5},$$

$$k_1(343 \text{ K}) = (1.3 \pm 0.4) \times 10^{-3}.$$

Based on these data, we determined the temperature dependence of  $k_1$  in the following form (the activation energy  $E_1$  is expressed in kJ/mol):

$$k_1, \text{l mol}^{-1} \text{s}^{-1} = 10^{10.8 \pm 1.5} \exp(-(90 \pm 7)/RT).$$

The slope of the straight lines in Fig. 5 ( $\tan \varphi = 0.5 k_3^2/k_4$ ; see Eq. (6)) makes it possible to find the  $k_3$  value because the rate constant for reaction (IV) is known:  $k_4 = (8 \pm 2) \times 10^8 \text{ l mol}^{-1} \text{s}^{-1}$  at  $T = 298 \text{ K}$  (toluene-di-*tert*-butyl peroxide (85 : 15 vol %) medium [18]). Assuming that the  $k_4$  values in this medium and

in chlorobenzene are the same and that  $k_4$  is invariable between 298 and 343 K, we have ( $\text{l mol}^{-1} \text{s}^{-1}$ )

$$k_3(298 \text{ K}) = (1.0 \pm 0.12) \times 10^8,$$

$$k_3(343 \text{ K}) = (1.0 \pm 0.13) \times 10^8.$$

Knowing  $k_1$  and  $k_3$  and using the value of  $k_v/(k_1 k_2 k_3)$  (see above), we obtain

$$\begin{aligned} k_v/k_2(298 \text{ K}) &= \beta_{298} = 31.0 \pm 10.8, \\ k_v/k_2(343 \text{ K}) &= \beta_{343} = 19.9 \pm 9.8. \end{aligned} \quad (7)$$

**Reaction order with respect to the components and the chain length.** The chain mechanism accounts for the fractional reaction orders with respect to the components. According to Eq. (4), the reaction rate  $w_{\text{QDI}}$  at  $w_i = 0$  is

$$w_{\text{QDI}} = k_1^{1/2} k_3 \frac{[\text{QDI}][\text{Ar}(\text{OH})_2]^{3/2}}{(k_4[\text{QDI}] + k_3(k_v/k_2)[\text{Ar}(\text{OH})_2])^{1/2}}.$$

It follows from this relationship that, in the absence of the initiator, the expected  $n_{\text{QDI}}$  and  $n_{\text{Ar}(\text{OH})_2}$  values lie in the ranges of  $0.5 < n_{\text{QDI}} < 1$  and  $1 < n_{\text{Ar}(\text{OH})_2} < 1.5$ . The experimental data presented above agree with this inference.

The reaction chain length  $\nu$  can be calculated as the average number of QDI molecules converted into  $\text{H}_2\text{QDI}$  per radical formed in the system:

$$\begin{aligned} \nu &= \frac{w_{\text{QDI}}}{w_{i\Sigma}} = \frac{k_3[\text{Ar}(\text{OH})_2]}{2(k_1[\text{QDI}][\text{Ar}(\text{OH})_2] + 0.5 w_i)^{1/2}} \\ &\times \left( \frac{[\text{QDI}]}{k_4[\text{QDI}] + k_3(k_v/k_2)[\text{Ar}(\text{OH})_2]} \right)^{1/2}, \end{aligned} \quad (8)$$



**Table 1.** Effects of the reactants and initiator concentrations and temperature on the initial reaction rate  $w_{\text{QDI}}$  and chain length  $v^*$ 

$[\text{QDI}]_0 \times 10^4$	$[\text{Ar}(\text{OH})_2]_0 \times 10^4$	$w_i \times 10^{12}$	$w_{\text{QDI}} \times 10^7$	$v_{\text{exp}}^{**} \times 10^{-5}$	$v_{\text{calc}}^{***} \times 10^{-5}$
$T = 298 \text{ K}$					
0.900	0.900	0	0.40	2.22	2.41
0.900	0.900	0.88	1.09	1.03	0.990
0.900	0.900	4.38	2.16	0.47	0.480
0.900	6.30	0	3.33	2.67	2.66
6.30	0.900	0	2.24	1.79	1.62
3.60	2.70	0	4.82	2.25	2.34
3.60	2.70	0.88	6.25	2.07	1.97
3.60	2.70	5.28	10.2	1.37	1.25
$T = 343 \text{ K}$					
0.861	0.861	0	5.83	0.302	0.263
0.861	0.861	412	27.0	0.063	0.056
0.861	0.861	824	33.5	0.040	0.040
0.861	3.44	0	22.6	0.293	0.296
3.44	0.861	0	19.1	0.248	0.192
3.44	2.58	0	58.1	0.252	0.251
3.44	2.58	412	95.9	0.149	0.150
3.44	2.58	824	127	0.120	0.117

\* The concentrations and rates are in mol/l and  $\text{mol l}^{-1} \text{s}^{-1}$ , respectively. Chlorobenzene, argon bubbling.

$$** v_{\text{exp}} = \frac{w_{\text{QDI}}}{2k_1[\text{QDI}]_0[\text{Ar}(\text{OH})_2]_0 + w_i}.$$

\*\*\*  $v_{\text{calc}}$  was calculated using formula (8).

where  $w_{i\Sigma}$  is the total rate of radical formation in the system. The calculated  $v$  values are listed in Table 1. In the absence of the initiator, the chain length is several hundreds of thousands of units at  $T = 298 \text{ K}$  and several tens of thousands of units at  $T = 343 \text{ K}$ , depending on the reactant concentrations. In the presence of the initiator,  $v$  is smaller because of the higher radical concentration in the system.

**Dependence of the reaction rate  $w_{\text{QDI}}$  on the  $\text{H}_2\text{QDI}$  concentration.** In the presence of  $\text{H}_2\text{QDI}$  in the system, backward reactions (–III) and (–IV) begin immediately. The rate of either backward reaction is

proportional to  $[\text{H}_2\text{QDI}]_0$ . Reactions (–III) and (–IV) exert opposite effects on the overall reaction rate  $w_{\text{QDI}}$ . Reaction (–III) decreases  $w_{\text{QDI}}$  because of the decrease in the chain length. Conversely, reaction (–IV) generates radicals and thus increases  $w_{\text{QDI}}$ . The dual (retarding and accelerating) effect of  $\text{H}_2\text{QDI}$  can be the cause of the experimentally observed extremum of  $w_{\text{QDI}}$  as a function of  $[\text{H}_2\text{QDI}]_0$  [2].

Some experimental plots of  $w_{\text{QDI}}$  versus  $[\text{H}_2\text{QDI}]_0$  are shown in Fig. 6. These plots are complicated curves with a maximum. The expression for the reaction rate in the presence of  $\text{H}_2\text{QDI}$  has the following form [2]:

$$w_{\text{QDI}} = k_2 k_3 [\text{Ar}(\text{OH})_2] [\text{QDI}]^{3/2} \times \left( \frac{k_1 [\text{Ar}(\text{OH})_2] + k_{-4} [\text{H}_2\text{QDI}]}{k_4 (k_2 [\text{QDI}] + k_{-3} [\text{H}_2\text{QDI}])^2 + k_3 k_v [\text{Ar}(\text{OH})_2] (k_2 [\text{QDI}] + k_{-3} [\text{H}_2\text{QDI}])} \right)^{1/2}. \quad (9)$$

Equation (9) was obtained under the assumption that step (VI) ( $\text{Ar}(\text{OH})\text{O}^\bullet$  disproportionation) can be ignored. It was mentioned above that the role of

step (VI) is small even in the reaction between QDI and  $\text{Ar}(\text{OH})_2$  in the absence of  $\text{H}_2\text{QDI}$  (see Eq. (V) and Fig. 4). In the presence of  $\text{H}_2\text{QDI}$ , this reaction can be

ignored even more safely because  $\text{H}_2\text{QDI}$  decreases the  $\text{Ar}(\text{OH})\text{O}^\bullet$  concentration, thus further diminishing the contribution from reaction (VI).

Since  $k_v$  and  $k_2$  are interrelated by Eq. (7), Eq. (9) actually contains not four, but three unknowns,

namely,  $k_2$ ,  $k_{-4}$ , and  $k_{-3}$ , which can be found by iterative fitting of the dependences of  $w_{\text{QDI}}$  on  $[\text{H}_2\text{QDI}]_0$  to Eq. (9). We performed these calculations, and the results obtained for selected dependences at 298 K are given below:

$[\text{QDI}] \times 10^4, \text{ mol/l}$	$[\text{Ar}(\text{OH}_2)] \times 10^4, \text{ mol/l}$	$k_2 \times 10^{-6}, \text{ l mol}^{-1} \text{ s}^{-1}$	$k_{-4} \times 10^5, \text{ l mol}^{-1} \text{ s}^{-1}$	$k_{-3} \times 10^{-6}, \text{ l mol}^{-1} \text{ s}^{-1}$
0.90	0.90	$8.1 \pm 1.4$	$1.6 \pm 0.8$	$1.3 \pm 0.5$
1.80	0.90	$9.5 \pm 4.2$	$1.5 \pm 0.6$	$1.3 \pm 0.4$
1.80	1.80	$7.4 \pm 2.7$	$1.7 \pm 0.9$	$1.1 \pm 0.3$

The true errors in the  $k_2$ ,  $k_{-4}$ , and  $k_{-3}$  values thus determined are larger than the dispersions of these values because of the wide spread of the absolute values of  $k_2$  and  $k_{-4}$  (as well as  $k_{-3}$ ); the low accuracy of the  $k_1$ ,  $k_3$ ,  $k_4$ , and  $\beta$  values used in the calculations; and the small number and insufficiently high accuracy of the experimental points. This is the likely reason why we faced the problem of solution multiplicity when fitting the less accurate data at 343 K to formula (9) and obtained  $k_2$ ,  $k_{-4}$ , and  $k_{-3}$  values with very large errors. For instance, the errors in  $k_{-4}$  are comparable with the  $k_{-4}$  value itself and the errors in  $k_2$  and  $k_{-3}$  exceed the  $k_2$  and  $k_{-3}$  values themselves by more than one order of magnitude.

To circumvent the difficulties, we reduced the number of sought rate constants by unity. We noticed that the  $k_2$  values obtained by fitting the  $w_{\text{QDI}}$  versus  $[\text{H}_2\text{QDI}]_0$  data at 298 K to formula (9) (when seeking all the three constants  $k_2$ ,  $k_{-4}$ , and  $k_{-3}$ ) lie in a comparatively narrow interval of  $(7\text{--}11) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ . Taking into account this fact, we set the  $k_v$  value between 298 and 343 K to be  $k_v = 3 \pm 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , which is the rounded value of  $k_v = \beta_{298}k_2$  at 298 K (see Eq. (7)). An analysis of published data [12, 18, 19] shows that the rate constants of the disproportionation of semiquinone radicals vary within 1.5–2 orders of magnitude and the value of  $3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  can be considered as their average value. Note that, in earlier works [1, 3, 5, 6, 14], we used a similar value of  $k_v = 4 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$  for analogous purposes.

Accepting  $k_v = 3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , we obtain from Eqs. (7) that  $k_2(298 \text{ K}) = (9.7 \pm 3.4) \times 10^6$  and  $k_2(343 \text{ K}) = (1.5 \pm 0.7) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$  ( $A \sim 3 \times 10^8$ ,  $E_2 \sim 8 \text{ kJ/mol}$ ).

Using the  $k_1 - k_4$  and  $k_v$  values, we reprocessed the experimental dependences of  $w_{\text{QDI}}$  on  $[\text{H}_2\text{QDI}]_0$  by fitting only the rate constants  $k_{-3}$  and  $k_{-4}$ . The results are presented in Table 2. The averaged values are given below ( $\text{l mol}^{-1} \text{ s}^{-1}$ ):

$$\begin{aligned} k_{-3}(298 \text{ K}) &= (1.4 \pm 0.4) \times 10^6, \\ k_{-3}(343 \text{ K}) &= (3.3 \pm 0.8) \times 10^6 \\ (A \sim 1 \times 10^9, E_{-3} \sim 16 \text{ kJ/mol}); \\ k_{-4}(298 \text{ K}) &= (1.6 \pm 0.6) \times 10^{-5}, \\ k_{-4}(343 \text{ K}) &= (1.56 \pm 0.5) \times 10^{-3} \\ (A \sim 2.3 \times 10^{10}, E_{-4} \sim 87 \text{ kJ/mol}). \end{aligned}$$

**Dependence of the reaction rate ( $w_{\text{QDI}}$ ) on the 2,5-dichloroquinone (Q) concentration.** According to the above reaction mechanism, the effect of Q on  $w_{\text{QDI}}$  should be similar to the effect of  $\text{H}_2\text{QDI}$ . In the presence of Q, backward reactions (–II) and (–VI) begin immediately and their rates increase as  $[\text{Q}]_0$  is increased. Reaction (–II) decreases  $w_{\text{QDI}}$  because of chain shortening, and reaction (–VI) increases  $w_{\text{QDI}}$  due to the increase in the chain initiation rate. The experimental plots of  $w_{\text{QDI}}$  versus  $[\text{Q}]_0$  at  $T = 298 \text{ K}$  are shown as an example in Fig. 7.

The expression for the reaction rate in the presence of Q has the following form [14]:

$$w_{\text{QDI}} = k_2 k_3 [\text{Ar}(\text{OH})_2]^{3/2} [\text{QDI}] \times \left( \frac{k_1 [\text{QDI}] + k_{-6} [\text{Q}]}{k_4 k_2^2 [\text{QDI}]^2 + k_v k_2 [\text{QDI}] (k_{-2} [\text{Q}] + k_3 [\text{Ar}(\text{OH})_2]) + k_6 (k_{-2} [\text{Q}] + k_3 [\text{Ar}(\text{OH})_2])^2} \right)^{1/2}. \quad (10)$$

**Table 2.** Reaction rate constants  $k_{-3}$  and  $k_{-4}$  determined by iterative fitting of the experimental dependences of  $w_{\text{QDI}}$  on  $[\text{H}_2\text{QDI}]_0^*$  to formula (9)

Experimental series	Constant concentrations in the series, mol/l		$k_{-3} \times 10^{-6}$ , $\text{l mol}^{-1} \text{ s}^{-1}$	$k_{-4} \times 10^4$ , $\text{l mol}^{-1} \text{ s}^{-1}$
	$[\text{QDI}]_0 \times 10^4$	$[\text{Ar}(\text{OH})_2]_0 \times 10^4$		
$T = 298 \text{ K}$				
1	3.60	3.60	$1.6 \pm 0.6$	$0.18 \pm 0.07$
2	3.60	1.80	$1.5 \pm 0.7$	$0.19 \pm 0.09$
3	1.80	1.80	$1.2 \pm 0.4$	$0.12 \pm 0.03$
4	1.80	0.90	$1.3 \pm 0.2$	$0.14 \pm 0.02$
5	0.90	0.90	$1.6 \pm 0.2$	$0.15 \pm 0.03$
$T = 343 \text{ K}$				
1	1.72	1.72	$3.3 \pm 1.0$	$16.2 \pm 5.8$
2	3.44	1.72	$3.9 \pm 1.1$	$14.2 \pm 4.4$
3	1.72	0.86	$2.8 \pm 0.5$	$16.5 \pm 3.5$

\* The rate constants fixed in the iterations ( $\text{l mol}^{-1} \text{s}^{-1}$ ):  $k_1 = 1.1 \times 10^{-5}$ ,  $k_2 = 9.7 \times 10^6$ ,  $k_3 = 1 \times 10^8$ ,  $k_4 = 8 \times 10^8$ , and  $k_V = 3 \times 10^8$  at  $T = 298 \text{ K}$ ;  $k_1 = 1.3 \times 10^{-3}$ ,  $k_2 = 1.5 \times 10^7$ ,  $k_3 = 1 \times 10^8$ ,  $k_4 = 8 \times 10^8$ , and  $k_V = 3 \times 10^8$  at  $T = 343 \text{ K}$ .

When deriving Eq. (10), we took into account reaction (VI), and, accordingly, this equation contains three unknown rate constants:  $k_{-2}$ ,  $k_{-6}$ , and  $k_6$ . However,  $k_{-2}$  ( $\text{l mol}^{-1} \text{s}^{-1}$ ) can be calculated using the above data and the following relationship [20]:

$$K_{\text{eq}} = K_2 K_3,$$

$$k_{-2}(298 \text{ K}) = (7.5 \pm 4) \times 10^6,$$

$$k_{-2}(343 \text{ K}) = (9.1 \pm 5) \times 10^6.$$

This yields the following values:

$$A \sim 3 \times 10^7, E_{-2} \sim \text{kJ/mol}.$$

This makes it possible to reduce the number of unknown constants to two.

We fitted the experimental data presented in Fig. 7 to formula (10) by an iteration method to determine only the unknowns  $k_{-6}$  and  $k_6$ . The results are listed in Table 3. As can be seen, the averaged  $k$  values ( $\text{l mol}^{-1} \text{s}^{-1}$ ) given below have a large error. Moreover, the  $k_6$  data should be considered only as tentative.

$$k_{-6}(298 \text{ K}) = (4.8 \pm 1.1) \times 10^{-6},$$

$$k_{-6}(343 \text{ K}) = (2.7 \pm 1.7) \times 10^{-4}$$

$$(A \sim 1 \times 10^8, E_{-3} \sim 76 \text{ kJ/mol});$$

$$k_6(298 \text{ K}) = (2.2 \pm 2.4) \times 10^6,$$

$$k_6(343 \text{ K}) = (5.5 \pm 7) \times 10^6$$

$$(A \sim 10^9, E_{-4} \sim 15 \text{ kJ/mol}).$$

**Experimental data for equal reactant concentrations.** According to Eq. (4), in the absence of the initiator, the expression for the reaction rate at a negligible contribution from reaction (VI) can be written as

$$w_{\text{QDI}} = \left( \frac{k_1 k_2 k_3^2 [\text{QDI}]^2 [\text{Ar}(\text{OH})_2]^3}{k_2 k_4 [\text{QDI}] + k_3 k_V [\text{Ar}(\text{OH})_2]} \right)^{1/2}.$$

At equal concentrations of  $[\text{QDI}]_0 = [\text{Ar}(\text{OH})_2]_0 = c$ , we have

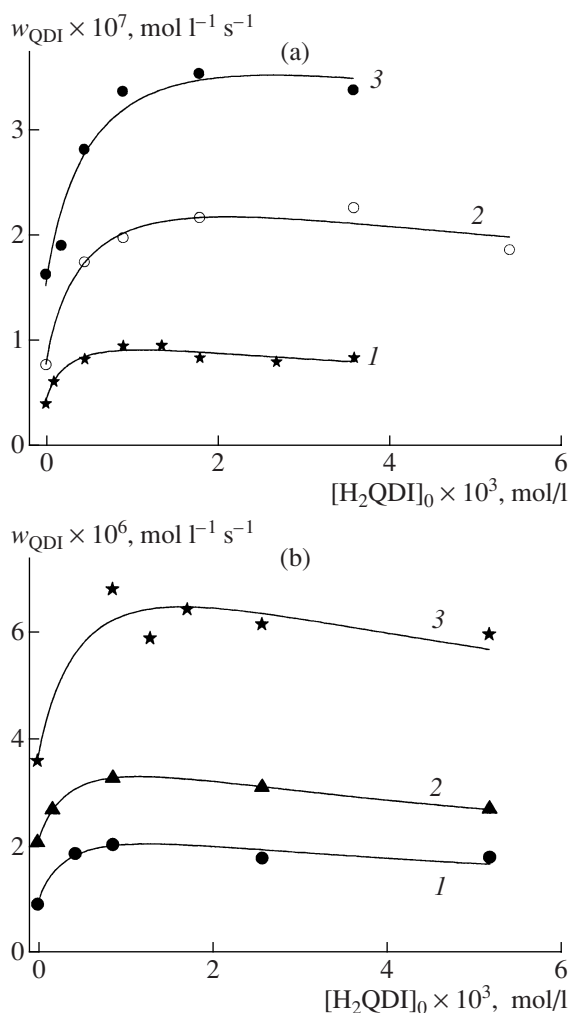
$$\begin{aligned} w_{\text{QDI}} &= \left( \frac{k_1 k_2 k_3^2}{k_2 k_4 + k_3 k_V} \right)^{1/2} c^2 \\ &= \left( \frac{k_1 k_3^2}{k_4 + k_3 (k_V/k_2)} \right)^{1/2} c^2 = \gamma c^2. \end{aligned} \quad (11)$$

It follows from Eq. (11) that the initial reaction rate  $w_{\text{QDI}}$  is proportional to the square of  $[\text{QDI}] = [\text{Ar}(\text{OH})_2]$ . Figure 8 presents experimental data confirming this inference. The  $\gamma$  values ( $\text{l mol}^{-1} \text{s}^{-1}$ ) obtained are given below:

$$\gamma_{\text{exp}}(298 \text{ K}) = 5.20 \pm 0.06, \quad \gamma_{\text{exp}}(343 \text{ K}) = 65.5 \pm 1.0.$$

These  $\gamma_{\text{exp}}$  values can be compared to the  $\gamma_{\text{calc}}$  values obtained by substituting the experimental rate constants  $k_1$ ,  $k_3$ ,  $k_4$ , and  $k_V/k_2$  into Eq. (11). With the errors



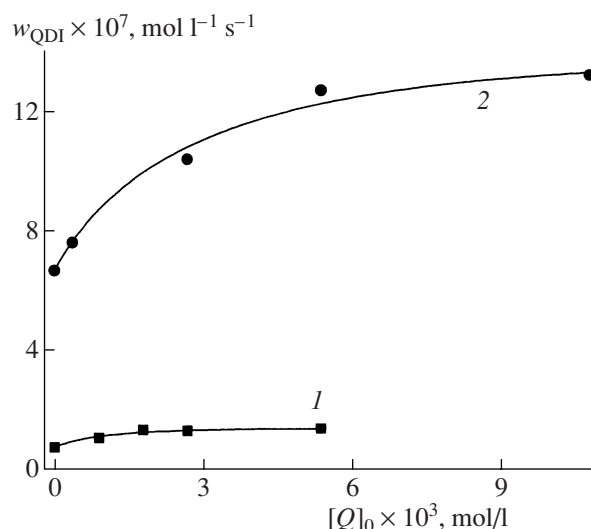


**Fig. 6.** Initial rate of the reaction between QDI and  $\text{Ar(OH)}_2$  versus  $\text{H}_2\text{QDI}$  concentration. (a)  $T = 298 \text{ K}$ ; the QDI and  $\text{Ar(OH)}_2$  concentrations ( $\times 10^4, \text{ mol/l}$ ) are (1) 0.90 and 0.90, (2) 1.80 and 0.90, and (3) 1.80 and 1.80, respectively. The points represent experimental data, and the lines are iterative fits to formula (9) at  $k_V/k_2 = \beta_{298} = 31.0$  and preset rate constant values of  $k_1 = 1.1 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_3 = 1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , and  $k_4 = 8 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ . (b)  $T = 343 \text{ K}$ ; the QDI and  $\text{Ar(OH)}_2$  concentrations ( $\times 10^4, \text{ mol/l}$ ) are (1) 1.72 and 0.86, (2) 1.72 and 1.72, and (3) 3.44 and 1.72, respectively. The points represent experimental data, and the lines are iterative fits to formula (9) at preset rate constant values of  $k_1 = 1.3 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_2 = 1.5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_3 = 1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ ,  $k_4 = 8 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ , and  $k_V = 3 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ .

ignored, this substitution yields the following values ( $\text{l mol}^{-1} \text{ s}^{-1}$ ):

$$\gamma_{\text{calc}} (298 \text{ K}) = 5.31 \text{ and } \gamma_{\text{calc}} (343 \text{ K}) = 68.3.$$

It can be seen that  $\gamma_{\text{calc}}$  and  $\gamma_{\text{exp}}$  are in agreement at both temperatures.



**Fig. 7.** Initial rate of the reaction between QDI and  $\text{Ar(OH)}_2$  versus the 2,5-dichloroquinone ( $\text{Q}$ ) concentration. The QDI and  $\text{Ar(OH)}_2$  concentrations ( $\times 10^4, \text{ mol/l}$ ) are (1) 1.80 and 0.90, respectively; (2) 3.60 and 3.60, respectively. The points represent experimental data, and the lines are iterative fits to formula (10). Reaction conditions: chlorobenzene,  $T = 298 \text{ K}$ , argon bubbling.

At equal concentrations of the starting reactants in the presence of  $\text{H}_2\text{QDI}$ , the reaction rate should increase in proportion to their squared concentration. Indeed, at  $[\text{QDI}]_0 = [\text{Ar(OH)}_2]_0 = [\text{H}_2\text{QDI}]_0 = c$  Eq. (9) can be rewritten as follows:

$$w_{\text{DQI}} = k_2 k_3 \left( \frac{k_1 + k_{-4}}{k_4 (k_2 + k_{-3})^2 + k_3 k_V (k_2 + k_{-3})} \right)^{1/2} c^2 = \delta c^2. \quad (12)$$

We carried out the corresponding experiments, and their results are presented in Fig. 8. Clearly, Eq. (12) agrees with the experimental data. The  $\delta$  values ( $\text{l mol}^{-1} \text{ s}^{-1}$ ) derived from the data presented in Fig. 8 are given below

$$\delta_{\text{exp}} (298 \text{ K}) = 7.09 \pm 0.49,$$

$$\delta_{\text{exp}} (343 \text{ K}) = 81.8 \pm 1.8.$$

The  $\delta_{\text{exp}}$  values can be compared to the  $\delta_{\text{calc}}$  values obtained by the substitution of the experimental rate constants into Eq. (12). The resulting  $\delta_{\text{calc}}$  values ( $\text{l mol}^{-1} \text{ s}^{-1}$ ) without errors are presented below:

$$\delta_{\text{calc}} (298 \text{ K}) = 7.67 \text{ and } \delta_{\text{calc}} (343 \text{ K}) = 88.8.$$

At both temperatures,  $\delta_{\text{calc}}$  is somewhat larger than  $\delta_{\text{exp}}$ . Since the  $\delta_{\text{exp}}$  values were determined with a comparatively high accuracy, the discrepancy between  $\delta_{\text{exp}}$  and  $\delta_{\text{calc}}$  is likely due to the low accuracy of the  $k_2$ ,  $k_{-3}$ ,  $k_{-4}$ , and  $k_V$  values.

**Table 3.** Reaction rate constants  $k_{-6}$  and  $k_6$  determined by iterative fitting of the experimental dependences of  $w_{\text{QDI}}$  on  $[Q]_0^*$  to formula (10)

Experimental series	Constant concentrations in the series, mol/l		$k_{-6} \times 10^6$ , l mol <sup>-1</sup> s <sup>-1</sup>	$k_6 \times 10^{-6}$ , l mol <sup>-1</sup> s <sup>-1</sup>
	[QDI] <sub>0</sub> × 10 <sup>4</sup>	[Ar(OH) <sub>2</sub> ] <sub>0</sub> × 10 <sup>4</sup>		
$T = 298 \text{ K}$				
1	1.80	0.90	5.1 ± 0.8	2.3 ± 2.7
2	3.60	3.60	4.3 ± 0.7	2.1 ± 2.2
$T = 343 \text{ K}$				
1	0.86	0.86	280 ± 190	7.4 ± 11.5
2	2.58	2.58	260 ± 65	3.9 ± 4.6

\* The rate constants fixed in the iterations (l mol<sup>-1</sup> s<sup>-1</sup>):  $k_1 = 1.1 \times 10^{-5}$ ,  $k_2 = 9.7 \times 10^6$ ,  $k_{-2} = 7.5 \times 10^6$ ,  $k_3 = 1 \times 10^8$ ,  $k_4 = 8 \times 10^8$ , and  $k_V = 3 \times 10^8$  at  $T = 298 \text{ K}$ ;  $k_1 = 1.3 \times 10^{-3}$ ,  $k_2 = 1.5 \times 10^7$ ,  $k_{-2} = 9.1 \times 10^6$ ,  $k_3 = 1 \times 10^8$ ,  $k_4 = 8 \times 10^8$ , and  $k_V = 3 \times 10^8$  at  $T = 343 \text{ K}$ .

At equal concentrations of  $[QDI]_0 = [Ar(OH)_2]_0 = [Q]_0 = c$ , the reaction rate  $w_{\text{QDI}}$  must also increase in proportion to the squared concentration. Indeed, at  $[Q]_0 = [Ar(OH)_2]_0 = [H_2QDI]_0 = c$ , Eq. (10) can be rewritten as

$$w_{\text{QDI}} = k_2 k_3 \left( \frac{k_1 + k_{-6}}{k_4 k_2^2 + k_2 k_V (k_{-2} + k_3) + k_6 (k_{-2} + k_3)^2} \right)^{1/2} c^2 = \delta c^2. \quad (13)$$

Relevant experimental data are presented in Fig. 8. It can be seen that Eq. (13) agrees with the experimental data. The  $\delta$  values derived from the data presented in Fig. 8 are given below:

$$\delta_{\text{exp}}(298 \text{ K}) = 5.95 \pm 0.17, \quad \delta_{\text{exp}}(343 \text{ K}) = 68.1 \pm 0.9.$$

At both temperatures,  $\delta_{\text{calc}}$  checks well with  $\delta_{\text{exp}}$ .

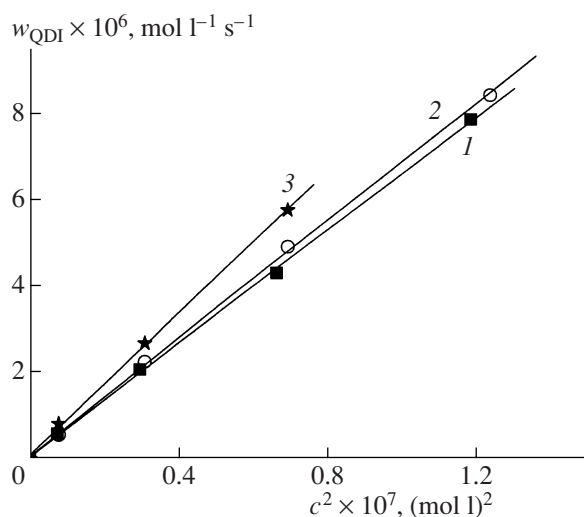
$$\delta_{\text{calc}}(298 \text{ K}) = 6.00 \quad \text{and} \quad \delta_{\text{calc}}(343 \text{ K}) = 69.3.$$

**Long time required for the establishment of the steady-state radical concentrations as the cause of the induction periods.** In the present work, we observed, for the first time, autoacceleration periods at the early stages of the reactions in the quinoneimine + hydroquinone systems. Since the reaction between QDI and  $Ar(OH)_2$  takes place via a chain mechanism, the induction periods can be due to the presence of inhibiting impurities. Because of this, prior to performing kinetic experiments, we further purified the reactants and the solvent. Special attention was given to the purity of  $Ar(OH)_2$  synthesized by us. The latter was multiply recrystallized from methanol–water and ethyl acetate–benzene mixtures and toluene. In addition, the compound was purified by passing its solutions through a chromatographic column (column length of 20 cm, column diameter of 2.5 cm,  $SiO_2$ -L (Chemapol), size fraction of 40–100  $\mu\text{m}$ , 30% ethyl acetate in benzene as the eluent, detection at  $\lambda = 300 \text{ nm}$ ) and collecting  $Ar(OH)_2$  in its chromatographic zone. Owing to this additional purification, the duration of the induction periods shortened, but by a factor no larger than 2.

We believe that the induction periods that are not caused by the impurities are due to the slow establishment of the steady-state radical concentration.  $T = 298 \text{ K}$ ,  $w_i = 0$ ,  $[QDI]_0 = [Ar(OH)_2]_0 = 9 \times 10^{-5} \text{ mol/l}$ . Let us assume that, during the establishment of the steady-state radical concentration, the QDI and  $Ar(OH)_2$  concentrations change insignificantly and are equal to their initial values. From Eq. (3), taking into account relationship (1), we obtain

$$\begin{aligned} k_1 [QDI] [Ar(OH)_2] &= \left( k_4 \frac{k_2^2 [QDI]^2}{k_3^2 [Ar(OH)_2]^2} \right. \\ &\quad \left. + k_V \frac{k_2 [QDI]}{k_3 [Ar(OH)_2]} + k_6 \right) [Ar(OH)O^\bullet]^2 \\ &= 3.9 \times 10^7 [Ar(OH)O^\bullet]_{\text{st}}^2. \end{aligned}$$

Using this equation, we calculated the steady-state concentration of the radicals:  $[Ar(OH)O^\bullet]_{\text{st}} = 4.8 \times 10^{-11} \text{ mol/l}$ . It follows from Eq. (1) that  $[HQDI^\bullet]_{\text{st}} = 0.097 [Ar(OH)O^\bullet]_{\text{st}}$ ; i.e., the total concentration of the radicals in the steady state is  $[Ar(OH)O^\bullet]_{\text{st}} + [HQDI^\bullet]_{\text{st}} = 5.3 \times 10^{-11} \text{ mol/l}$ . Since the rate of radical formation in this system is  $w_{i(0)} = 2k_1 [QDI]_0 [Ar(OH)_2]_0 = 1.8 \times 10^{-13} \text{ mol l}^{-1} \text{ s}^{-1}$ , it follows from these data that, even if there is no radical decay in the system, the time required for the establishment of the steady-state radical concentration is  $\sim 300 \text{ s}$ .



**Fig. 8.** Linear plots of the reaction rate  $w_{\text{QDI}}$  versus the square of the equal concentrations of the reactants and final product admixtures: (1)  $[\text{QDI}]_0 = [\text{Ar}(\text{OH})_2]_0 = c$ , (2)  $[\text{DQI}]_0 = [\text{Ar}(\text{OH})_2]_0 = [\text{QI}]_0 = c$ , and (3)  $[\text{DQI}]_0 = [\text{Ar}(\text{OH})_2]_0 = [\text{H}_2\text{QDI}]_0 = c$  (chlorobenzene, 343 K, argon bubbling).

The earlier studied reactions of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-di-*tert*-butyl-, 2,5-dimethyl-, and 2,5-dichlorohydroquinones are characterized by substantially larger values of  $k_1$  (298 K) =  $3.2 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$  [1, 3],  $3.4 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$  [14], and  $3.5 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$  [5]. The concentration of either reactant in those studies was generally two times higher than the concentrations examined in similar experiments in this work (because the extinction coefficient of *N*-phenyl-1,4-benzoquinone monoimine is almost two times smaller than  $\epsilon_{\text{QDI}}$ ). Thus, the chain initiation rates were 2–3 orders of magnitude higher than those in the present study. Since the chain termination rate constant in the system examined differs only slightly from the same rate constants in the earlier studied systems, we can deduce that the induction periods in the latter systems are at least one order of magnitude shorter than those observed in the present work. This did not allow us to observe the induction periods in the reactions involving *N*-phenyl-1,4-benzoquinone monoimine.

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