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Estimation of Kinetic Parameters of Reversible Chain Reactions of Quinoneimines with Hydroquinones Having Self-Acceleration Periods

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Abstract—A new approach is suggested for determining the kinetic parameters and rate constants of the elementary steps of reversible chain reactions having self-acceleration periods due to the long time required for the concentrations of the chain-carrier radicals to reach their steady-state values. This approach is illustrated by the example of the reversible chain reaction between *N*,*N*'-diphenyl-1,4-benzoquinonediimine and 2,5-dichlorohydroquinone in chlorobenzene. The disappearance rate of one of the initial reactants, *N*,*N*'-diphenyl-1,4-benzoquinonediimine, at the inflection point of its disappearance curve, is considered as the basic kinetic characteristic of the reaction. The empirical function $y = a\exp(bt^c) + d$, where a, b, c, and d are the fitted parameters ($b < 0$, $c > 1$), is suggested for approximating the S-shaped kinetic curves and for calculating the reaction rate. The rate constants of the elementary steps are preferably derived from experimental data obtained at equal concentrations of the initial reactants, and also product additions when their effect on the reaction rate is studied. The effective rate constant of chain termination is derived from the time to reach the steady state. The results obtained in this way are compared with earlier data obtained using the "initial" reaction rates calculated by means of exponential approximation of portions of *N*,*N*'-diphenyl-1,4-benzoquinonediimine disappearance curves after the inflection point.

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The reactions of quinoneimines with hydroquinones proceed via a reversible chain mechanism both from the side of the initial compounds and from the side of the products [1–4]. These reactions were the first liquid-phase reversible chain reactions to be discovered. Only gas-phase reactions of this type had been known earlier [5–7].

These reactions have a number of specific features. They have no rate-limiting chain propagation step [1, 3, 8, 9]. It has recently been demonstrated by the example of the reaction between *N*,*N*'-diphenyl-1,4-benzoquinonediimine (QDI) and 2,5-dichlorohydroquinone ($Ar(OH)_2$) in chlorobenzene [10] that the reactions of quinoneimines with hydroquinones generally have an induction period. In the case of the chain reaction between QDI and $Ar(OH)_2$ (initial chain length of $\nu = 10^4$–10^5 units), the induction period is 3–5 min, depending on the experimental conditions [10, 11]. Determination of the rate constants of the elementary steps of a complex reaction with a self-acceleration period involves serious difficulties. Here, using the chain reaction between QDI and $Ar(OH)_2$ as an example, we suggest a new approach to this problem.

Detailed investigation of the reversible chain reactions of quinoneimines with hydroquinones is stimulated by the high significance of these reactions in practice. These reactions are similar to the quinone + hydroquinone reactions, and the latter are of great significance not only in chemistry, but also in biochemical applications since they play the key role in the protective action of quinone-type bioantioxidants (ubiquinone, vitamin K group) [12]. Quinones and quinoneimines result from the oxidative degradation of the most widespread phenolic (hydroquinone-type) and aromatic amine antioxidants [12–16] in oxidation reactions inhibited by these antioxidants. The reactions in which quinones and quinoneimines are involved under these conditions exert a marked effect on the total antioxidant efficiency of the individual initial phenolic and amine antioxidants and on that of their compositions [16, 17].

EXPERIMENTAL

The synthesis and purification of QDI, $Ar(OH)_2$, *N*,*N*'-diphenyl-1,4-phenylenediamine (H_2QDI), 2,5-dichloroquinone (Q), tetraphenylhydrazine (TPH) initiator) and chlorobenzene as the solvent were described earlier [18]. Reaction kinetics was studied as quinoneimine disappearance. Experiments were carried out at $T = 298 \pm 0.1$ in a temperature-controlled quartz bubbled cell built in a Specord UV-VIS spectrophotometer (cell volume of 8.5 ml, optical path

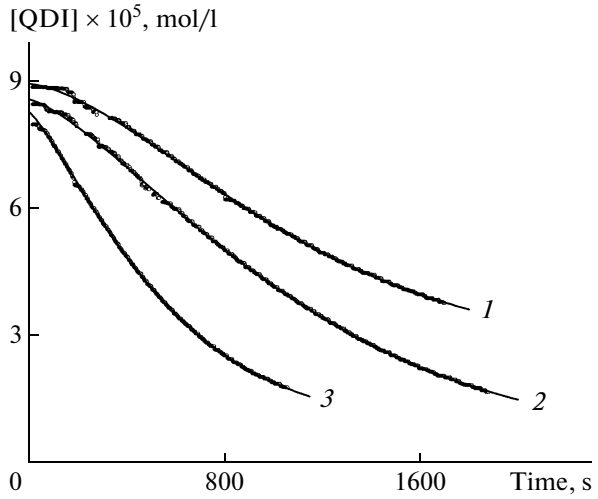


Fig. 1. QDI disappearance kinetics in the chain reaction between QDI and $Ar(OH)_2$ (*1*) in the absence and (*2*, *3*) in the presence of an initiator for different delay times (t_{delay}) between combining the $Ar(OH)_2$ solution with the initiator and adding QDI. In all runs, $[QDI]_0 = [Ar(OH)_2]_0 = 9.0 \times 10^{-5}$ mol/l. w_i = (*1*) 0 (uninitiated reaction) and 1.41×10^{-11} mol l^{-1} s^{-1}. t_{delay} = (*2*) 100 and (*3*) 950 s. The points represent experimental data, and the lines are the fits to formula (4). Chlorobenzene, 298 K.

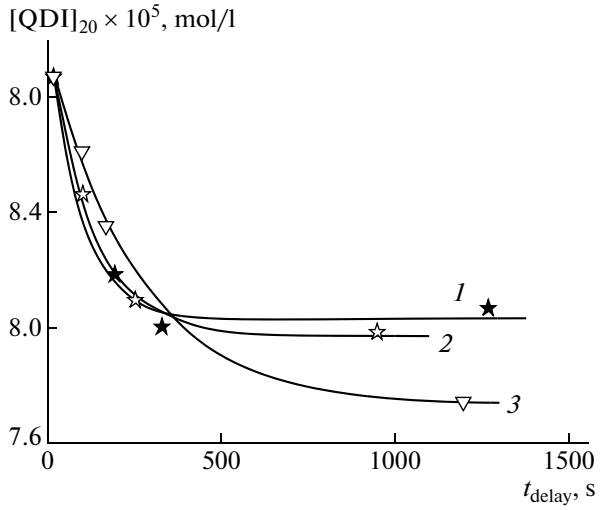


Fig. 2. Initial concentration $[QDI]_{20}$ as a function of the delay time t_{delay} between combining the $Ar(OH)_2$ solution with the initiator and the reaction onset (QDI addition). In all runs, $[QDI]_0 = [Ar(OH)_2]_0 = 9.0 \times 10^{-5}$ mol/l. $w_i \times 10^{11}$ = (*1*) 0.352, (*2*) 1.41, and (*3*) 2.11 mol l^{-1} s^{-1}. Chlorobenzene, 298 K, bubbling argon.

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 in the visible region, specifically, 22260, 20000, or 19000 cm^{-1}, depending on the initial QDI concentration, at intervals not longer than 1 s. The reaction product Q also absorbs, though weakly, in this region, but its absorption was neglected because of its small molar extinction coefficient ($\varepsilon_Q^{22260} \approx 20$ l mol^{-1} cm^{-1} versus $\varepsilon_{QDI}^{22260} \sim 7 \times 10^3$ l mol^{-1} cm^{-1}).

For technical reasons (time needed to pour the solution, to stir the contents of the reactor, to close the cell compartment, etc.), we began recording the QDI disappearance kinetics some time (on the average, 20 ± 3 s) after the addition of the second component and the onset of the reaction. This time was taken into account in the determination of induction periods.

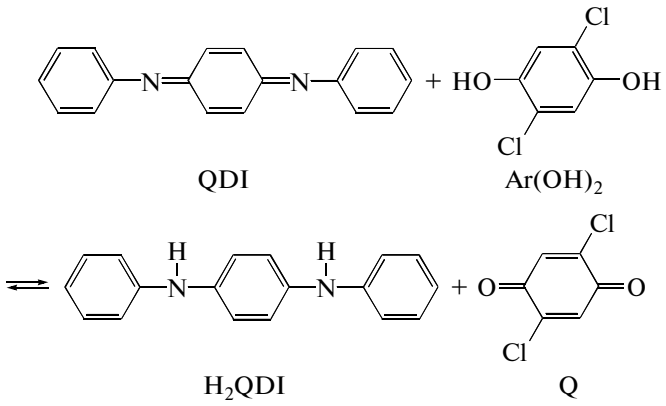
It was established by special-purpose experiments that the observed kinetic parameters of the reaction—initial quinoneimine concentration $[QDI]_{20}$ (measured after 20 s), reaction rate w_{QDI}, and induction period τ—depend on the experimental procedure, including the order in which the reactants and initiator were combined and the reactor charging time. If a solution of $Ar(OH)_2$ and the initiator is prepared in the reactor and then a QDI solution is added after some delay time (t_{delay}), the kinetics recorded immediately after that will depend on t_{delay}. It is possibly due to this specific feature that the QDI disappearance rate (w_{QDI}) values measured in replica experiments differ by a factor of 2–3 (Fig. 1, curves *2*, *3*). Likewise, the data presented in Fig. 2 demonstrate that $[QDI]_{20}$ initially falls rapidly as t_{delay} in increased, but for $t_{delay} >$ 400–600 s this effect is not observed any longer. This is due to the fact that, before the onset of the chain reaction, semiquinone radicals buildup in the solution containing $Ar(OH)_2$ and the initiator, their concentration exceeding the steady-state concentration $[Ar(OH)O^{\bullet}]_{st}$ for the chain reaction between QDI and $Ar(OH)_2$ (which starts after QDI addition) [11]. This inference is consistent with the simulated kinetics of this reaction [11].

No such dependence of w_{QDI} and $[QDI]_{20}$ on t_{delay} is observed when the QDI and initiator solutions are initially combined in the reactor, the mixed solution is held for the time t_{delay}, and the reaction is then started by adding an $Ar(OH)_2$ solution. For this reason, it is this order of reactant mixing that was used in the investigation of the reaction in the presence of the initiator, unless otherwise specified.

Significant data distortion might arise from the capability of the semiquinone radicals to react with O_2 [19–23]. For this reason, argon was bubbled though the solution both before and during the reaction.

RESULTS AND DISCUSSION

The reaction between QDI and $Ar(OH)_2$ proceeds according to the stoichiometric equation



$(s, -s)$

In this reaction, QDI is reduced to H_2QDI owing to the oxidation of $Ar(OH)_2$ into Q. The equilibrium constant of reaction $(s, -s)$ in chlorobenzene at 298 K is $K_{eq}^{298} = 92 \pm 13$ [18]. In view of this, the reversibility of the reaction can be neglected unless the products H_2QDI and Q are added. The mechanism of reaction $(s, -s)$ includes the following elementary steps [1, 10]:

(i)	TPH	$\longrightarrow Ph_2N^{\cdot}$	$\xrightarrow{Ar(OH)_2} Ar(OH)O^{\cdot}$	initiation
$(1, -1)$	$QDI + Ar(OH)_2$	$\rightleftharpoons$	$HQDI^{\cdot} + Ar(OH)O^{\cdot}$	chain initiation
$(2, -2)$	$QDI + Ar(OH)O^{\cdot}$	$\rightleftharpoons$	$HQDI^{\cdot} + Q$	chain propagation
$(3, -3)$	$HQDI^{\cdot} + Ar(OH)_2$	$\rightleftharpoons$	$H_2QDI + Ar(OH)O^{\cdot}$	"
$(4, -4)$	$HQDI^{\cdot} + HQDI^{\cdot}$	$\rightleftharpoons$	$H_2QDI + QDI$	chain termination
$(-1, 1)$	$HQDI^{\cdot} + Ar(OH)O^{\cdot}$	$\rightleftharpoons$	$QDI + Ar(OH)_2$	"
$(5, -5)$	$HQDI^{\cdot} + Ar(OH)O^{\cdot}$	$\rightleftharpoons$	$H_2QDI + Q$	"
$(6, -6)$	$Ar(OH)O^{\cdot} + Ar(OH)O^{\cdot}$	$\rightleftharpoons$	$Ar(OH)_2 + Q$	"

Scheme.

Here, $HQDI^{\cdot}$ and $Ar(OH)O^{\cdot}$ are the 4-anilinodiphenylaminyl and 2,5-dichloro-4-hydroxophenoxyl semiquinone radicals, which result from H_2QDI and $Ar(OH)_2$, respectively, via the abstraction of a hydrogen atom.

Figure 1 (curve *1*) indicates that the QDI disappearance kinetics is characterized by self-acceleration periods. It was mentioned above that, in the earlier studied reactions of quinoneimines with hydroquinones [1, 3, 8, 9], these periods were negligibly short and it was possible to derive kinetic parameters from initial rate (w_{QDI}) data. In order to determine w_{QDI}, the quinone diimine disappearance curves were fitted to the exponential function

$$[QDI] = a_1\exp(-b_1t) + c_1, \quad (1)$$

where a_1, b_1, and c_1 are the parameters fitted by iterations; $w_{QDI} = a_1b_1$.

In our earlier study [10], kinetic data for the reaction between QDI and $Ar(OH)_2$, which has self-acceleration periods, were fitted to a modification of function (1):

$$[QDI] = a_2\exp\{-b_2(t - \tau)\} + c_2. \quad (1a)$$

The "initial" reaction rate w_{QDI} was taken to be equal to the negative derivative of function (1a) at the point τ, at which it intersects the horizontal line indicating the preset initial concentration of the quinone diimine, $[QDI] = [QDI]_0$:

$$w_{QDI} = a_2b_2\exp\{-\ln a_2 - \ln([QDI]_0 - c_2)\}.$$

The parameters of function (1a) were determined by fitting, to formula (1a), portions of the QDI disappearance curve after the inflection point (medium and large extents of the reaction). Obviously, this way or processing kinetic data could provide only estimates of the parameters.

In this work, the *S*-shaped kinetic curves are fitted to the empirical function

$$[QDI] = a\exp(bt^c) + d, \quad (2)$$

where *a, b, c*, and *d* are the parameters fitted by iterations; $b < 0$; $c > 1$. Function (2) does not allow the initial reaction rate to be determined, because $(d[QDI]/dt)|_{t=0} = 0$, However, starting at fairly small extents of the reaction, this function provides a good fit to the observed curves up to the completion of the reaction (Fig. 1). Table 1 lists *a*, *b*, *c*, and *d* values for a number of initial reactant concentrations.

Table 1. Numerical values of the parameters a, b, c, and d of function (2) in several runs

$[QDI]_0 \times 10^4$	$[Ar(OH)_2]_0 \times 10^4$	$[H_2QDI]_0 \times 10^4$	$[Q]_0 \times 10^4$	$a \times 10^4$, mol/l	$b \times 10^4$, s^{-c}	c	$d \times 10^5$, mol/l
mol/l							
0.9	0.9	0	0	0.70 ± 0.01	−0.46 ± 0.01	1.41 ± 0.01	2.23 ± 0.01
1.8	1.8	0	0	1.47 ± 0.01	−0.38 ± 0.01	1.51 ± 0.01	4.00 ± 0.01
2.7	2.7	0	0	1.82 ± 0.01	−2.29 ± 0.1	1.33 ± 0.01	5.8 ± 0.1
0.9	0.9	9	0	0.50 ± 0.01	−11.6 ± 0.5	1.09 ± 0.01	4.28 ± 0.04
0.9	0.9	27	0	0.36 ± 0.01	−5.5 ± 0.5	1.22 ± 0.02	5.2 ± 0.1
0.9	0.9	36	0	0.36 ± 0.01	−5.85 ± 0.2	1.17 ± 0.01	4.69 ± 0.01
3.6	3.6	0	3.6	2.51 ± 0.01	−15.7 ± 0.3	1.08 ± 0.003	5.82 ± 0.01
3.6	3.6	0	27	2.19 ± 0.02	−32.5 ± 1.9	1.04 ± 0.01	9.5 ± 0.1
3.6	3.6	0	54	1.76 ± 0.01	−39.0 ± 2.2	1.05 ± 0.01	11.4 ± 0.1
3.6	3.6	0	108	1.53 ± 0.01	−53.2 ± 2.8	1.05 ± 0.01	16.4 ± 0.02

An advantage of function (2) is that its parameters are derived almost from the entire kinetic curve, including the initial portions of the curve before the inflection point. The coordinated of the inflection points are determined by differentiation:

$$t_{infl} = \exp\left(\frac{1}{c}\ln\frac{1-c}{bc}\right),$$
$$[QDI]_{infl} = a\exp(bt_{infl}^c) + d. \quad (3)$$

The QDI disappearance rate w_{QDI} at the inflection point of the curve defined by (2), with coordinates given by Eq. (3), will be used as the kinetic characteristic of the reaction. It was established experimentally that the QDI concentration at the inflection point is typically not lower than ~80% of $[QDI]_0$. At comparably large rate constants, this allows one to neglect the effect of the products and to consider w_{QDI} an analogue of the initial reaction rate at $t = 0$, but at the concentrations corresponding to the inflection point. The expression for w_{QDI} at the inflection point is obtained by differentiation of function (2):

$$w_{QDI} = -abc\exp(bt_{infl}^c) \times t_{infl}^{c-1}. \quad (4)$$

To calculate $[QDI]_{infl}$, we used Eq. (3), and the concentrations of the other compounds were calculated from their initial concentrations taking into account the $[QDI]_{infl}$ value and the stoichiometry of the reaction.

Under the assumption that, at $t = t_{infl}$, the reaction between QDI and $Ar(OH)_2$ proceeds in the steady-state regime, the expression for w_{QDI} appears as

$$k_1[QDI][Ar(OH)_2] + 0.5w_i = k_4[HQDI^\bullet]^2 + (k_{-1} + k_5)[HQDI^\bullet][Ar(OH)O^\bullet] + k_6[Ar(OH)O^\bullet]^2. \quad (5)$$

Let us express $[HQDI^\bullet]$ and $[Ar(OH)O^\bullet]$ from the equation

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

and substitute them into Eq. (5). We will obtain

$$w_{QDI}^2 = \frac{k_2^2k_3^2[QDI]^2[Ar(OH)_2]^2(k_1[QDI][Ar(OH)_2] + 0.5w_i)}{k_4k_2^2[QDI]^2 + k_Vk_2k_3[Ar(OH)_2][QDI] + k_6k_3^2[Ar(OH)_2]^2}, \quad (7)$$

where $k_V = k_{-1} + k_5$. The complexity of expression (7) for w_{QDI} is due to the fact that, on the right-hand side of Eq. (5), it is necessary to keep all of the four terms because of the absence of a rate-limiting chain propagation step.

The expression for w_{QDI} is much simpler in the case of equal reactant concentrations [3, 4, 10]. For this reason, most experiments in this study were performed under these conditions. At $[QDI]_{infl} = [Ar(OH)_2]_{infl}$, Eq. (7) can be written as

$$w_{QDI} = \frac{k_2}{\{k_4(k_2^2/k_3^2) + k_V(k_2/k_3) + k_6\}^{1/2}} \times [QDI]_{infl}\left(k_1[QDI]_{infl}^2 + 0.5w_i\right)^{1/2} = \frac{k_2}{(2k_{Ar(OH)O^\bullet}^{term})^{1/2}}[QDI]_{infl}w_{i\Sigma}^{1/2}. \quad (8)$$

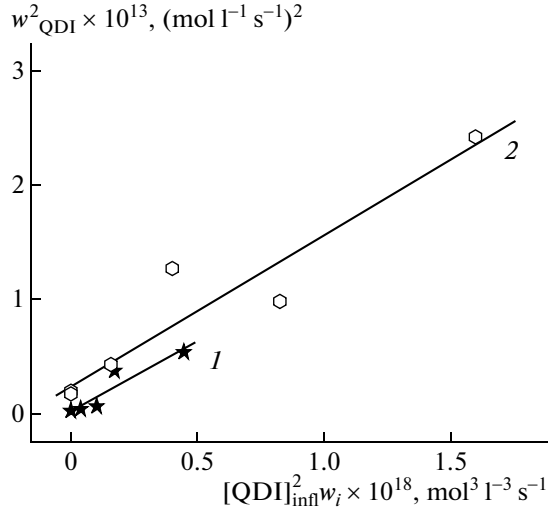


Fig. 3. Linear relationships between w^2_{QDI} and $[QDI]^2_{infl} w_i$ in the runs with equal initial reactant concentrations: $[QDI]_0 = [Ar(OH)_2]_0 =$ (*1*) 9.0×10^{-5} and (*2*) 1.8×10^{-4} mol/l. Chlorobenzene, 298 K, bubbling argon.

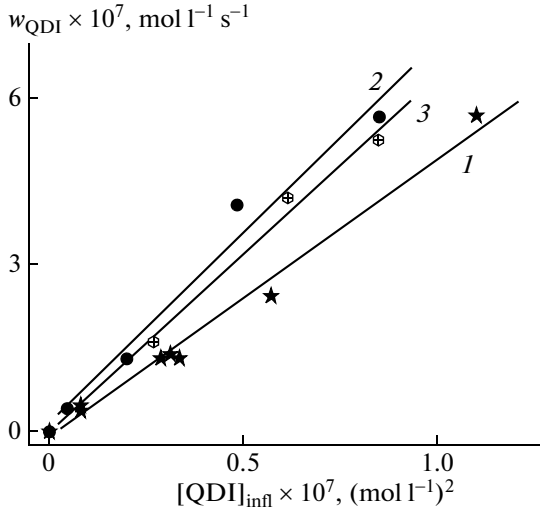


Fig. 4. w_{QDI} versus squared $[QDI]_{infl}$ at equal reactant concentrations: (*1*) no products added, $[QDI]_0 = [Ar(OH)_2]_0$; (*2*) $[QDI]_0 = [Ar(OH)_2]_0 = [H_2QDI]_0$; (*3*) $[QDI]_0 = [Ar(OH)_2]_0 = [Q]_0$. Chlorobenzene, 298 K, bubbling argon.

Here, it is taken into account that the total radical formation rate in the system is

$$w_{i\Sigma} = 2k_1[QDI]^2_{infl} + w_i,$$

and $k_4(k_2^2/k_3^2) + k_V(k_2/k_3) + k_6 = k^{term}_{Ar(OH)O^\cdot}$ is the effective rate constant of chain termination on the semiquinone radical $Ar(OH)O^\cdot$. Clearly, the equation for w_{QDI} at $[QDI]_{infl} = [Ar(OH)_2]_{infl}$ has the same form as the rate equation for nonbranched chain reactions with quadratic-law chain termination and a rate-limiting chain propagation step [24, 25].

Equation (8) can be represented as

$$w^2_{QDI} = \frac{k_1 k_2^2}{k^{term}_{Ar(OH)O^\cdot}}[QDI]^4_{infl} + \frac{k_2^2}{2k^{term}_{Ar(OH)O^\cdot}}[QDI]^2_{infl} w_i = A + B \times [QDI]^2_{infl} w_i. \quad (9)$$

Here, $[QDI]_{infl}$ stands for the equal QDI and $Ar(OH)_2$ concentrations at the inflection point of the QDI disappearance curve, calculated via Eq. (3). Since $[QDI]_{infl} \ll 1$, the first term A on the right-hand side of Eq. (9) can be neglected because it is small as compared to the second term. In addition, this makes it possible to take A to be constant, so there must be a linear relationship between w^2_{QDI} and $[QDI]^2_{infl} w_i$. As is demonstrated in Fig. 3, this inference is corroborated by experimental data. From the slope B of the straight lines in Fig. 3, we derive

$$k_2\left(k^{term}_{Ar(OH)O^\cdot}\right)^{1/2} = 500 \pm 50 \text{ (l mol}^{-1}\text{ s}^{-1})^{1/2}.$$

According to Eq. (9), in the absence of an initiator,

$$w_{QDI} = \frac{k_1^{1/2} k_2}{\left(k^{term}_{Ar(OH)O^\cdot}\right)^{1/2}}[QDI]^2_{infl}, \quad (10)$$

that is, the reaction rate w_{QDI} is proportional to the product of the equal concentrations [QDI] and $[Ar(OH)_2]$ (Fig. 4). From the slope of straight line *1* in Fig. 4, we find

$$\frac{k_1^{1/2} k_2}{\left(k^{term}_{Ar(OH)O^\cdot}\right)^{1/2}} = 5.0 \pm 0.2 \text{ l mol}^{-1}\text{ s}^{-1}.$$

From the above parameters, we obtain $k_1 = (9.7 \pm 2.6) \times 10^{-5}$ l mol^{-1} s^{-1}, which is almost one order of magnitude larger than the earlier reported value of $k_1 = 1.1 \times 10^{-5}$ l mol^{-1} s^{-1} [10].

In the absence of an initiator ($w_i = 0$), formula (7) reduces to

$$\frac{[QDI]_{infl}[Ar(OH)_2]^3_{infl}}{w^2_{QDI}} = \frac{k_4}{k_1 k_3^2} + \frac{k_V}{k_1 k_2 k_3}\frac{[Ar(OH)_2]_{infl}}{[QDI]_{infl}} + \frac{k_6}{k_1 k_2^2}\left(\frac{[Ar(OH)_2]_{infl}}{[QDI]_{infl}}\right)^2. \quad (11)$$

Figure 5 plots the dependence of $[QDI]_{infl}[Ar(OH)_2]^3_{infl}/w^2_{QDI}$ on $[Ar(OH)_2]_{infl}/[QDI]_{infl}$, which can be approximated by a straight line. Therefore, the last term on the right-hand side of Eq. (11) can be neglected. Because of the large error in the determination of the ordinate intercept, only the slopes of the straight lines (Fig. 5) were used in further

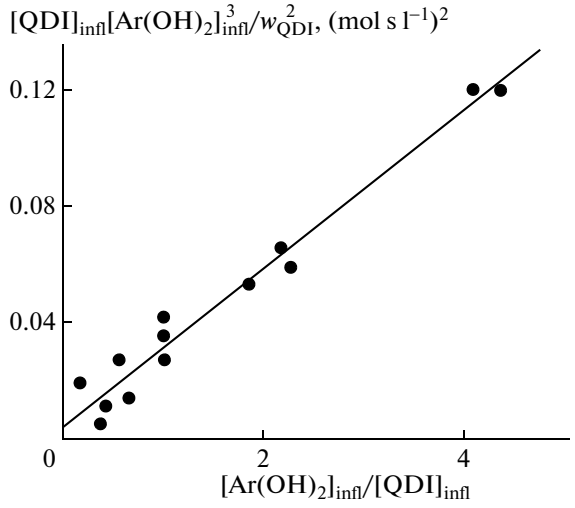


Fig. 5. Fitting experimental data obtained in the absence of an initiator to Eq, (11). Chlorobenzene, 298 K, bubbling argon.

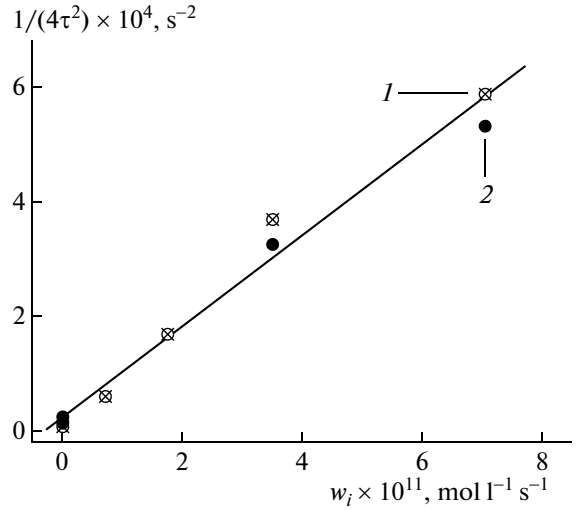


Fig. 6. $1/(4\tau^2)$ versus w_i for two series of runs at equal reactant concentration of $[QDI]_0 = [Ar(OH)_2]_0 = (1)$ 9.0×10^{-5} and (2) 1.8×10^{-4} mol/l.

calculations. This made it possible to determine the parameter

$$\frac{k_V}{k_1 k_2 k_3} = (2.70 \pm 0.14) \times 10^{-2} \text{ (mol s l}^{-1})^2.$$

Setting k_V to be 3×10^8 l mol^{-1} s^{-1} [10] and taking into account that $k_1 = (9.7 \pm 2.6) \times 10^{-5}$ l mol^{-1} s^{-1} (see above), we obtain, from this equality,

$$k_2 k_3 = (1.1 \pm 0.3) \times 10^{14} \text{ (l mol}^{-1} \text{ s}^{-1})^2.$$

The k_2 and k_3 values were earlier derived by combining data obtained in the presence and in the absence of an initiator [8–10]. Here, we suggest another procedure for this purpose.

To determine k_2, we will use the above value of $k_2/(k^{term}_{Ar(OH)O^{\cdot}})^{1/2} = 500 \pm 50$ (l mol^{-1} s^{-1})$^{1/2}$. The necessary quantitative estimate of $k^{term}_{Ar(OH)O^{\cdot}}$ can be derived from the self-acceleration period length as a function of the initiation rate w_i by performing a series of experiments at equal QDI and $Ar(OH)_2$ concentrations. The self-acceleration periods (Fig. 1) are largely due to the long time required for the establishment of the steady-state $HQDI^{\cdot}$ and $Ar(OH)O^{\cdot}$ concentrations in the system [10]. The concentrations of these radicals are related by expression (6). It is, therefore, possible to take into account only the variation of the concentration of one of them, e.g., $Ar(OH)O^{\cdot}$. At the early stages of the reaction without an initiator, immediately after combining the reactants, the concentration of this radical increases from 0 to its steady-state value $[Ar(OH)O^{\cdot}]_{st}$, and this is accompanied by an increase in the reaction rate. Assume that the time it takes for the steady-state concentration $[Ar(OH)O^{\cdot}]_{st}$ to be established, τ, is equal to the mean lifetime of the reaction chain in the steady state, $t_{ch} = (2k^{term}_{Ar(OH)O^{\cdot}} \times w_{i\Sigma})^{-1/2}$; that is, $\tau = t_{ch}$ [24, 25]. The time τ will be estimated as the abscissa of the intersection point between the horizontal line $[QDI] = [QDI]^{exp}_0$ and the tangent line

$$[QDI] = Mt + N \quad (12)$$

for the QDI disappearance curve (2) at its inflection point, whose coordinates are given by Eq. (3). Here, $M = -w_{QDI}$ and N is derived from the equation

$$[QDI]_{infl} = a\exp(bt^c_{infl}) + d = -w_{QDI}\tau + N,$$

whence it follows that

$$N = a\exp(bt^c_{infl}) + d + w_{QDI}\tau. \quad (13)$$

Therefore,

$$\tau = \frac{N - [QDI]^{exp}_0}{w_{QDI}}. \quad (14)$$

In view of this,

$$\tau = t_{ch} = \left(2k^{term}_{Ar(OH)O^{\cdot}} \cdot w_{i\Sigma}\right)^{-1/2}$$

$$= \left(2k^{term}_{Ar(OH)O^{\cdot}} \times (2k_1[QDI]^2_{infl} + w_i)\right)^{-1/2}$$

or

$$\frac{1}{4\tau^2} = k_1 k^{term}_{Ar(OH)O^{\cdot}} \cdot [QDI]^2_{infl} + 0.5k^{term}_{Ar(OH)O^{\cdot}} \cdot w_i. \quad (15)$$

Figure 6 illustrates the fit between the data of two series of measurements at equal reactant concentrations and formula (15). From the slope of the straight line in Fig. 6, we obtain

$$k^{term}_{Ar(OH)O^{\cdot}} = (1.6 \pm 0.1) \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}.$$

From this $k^{term}_{Ar(OH)O^{\cdot}}$ value and the above $k_2/(k^{term}_{Ar(OH)O^{\cdot}})^{1/2}$ value, we obtain

$$k_2 = (2.0 \pm 0.2) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}.$$

These $k^{term}_{Ar(OH)O^{\cdot}}$ and k_2 values differ from the earlier determined values $k^{term}_{Ar(OH)O^{\cdot}} = 3.9 \times 10^7$ l mol^{-1} s^{-1} and $k_2 = (9.7 \pm 3.4) \times 10^6$ l mol^{-1} s^{-1} [10]. The causes of this discrepancy were noted above. Firstly, the data obtained in the previous study and in this work were fitted to different functions—Eqs. (1) and (2). The second, most important cause is that, in the previous kinetic study of the reaction in the presence of the initiator, we attached no significance to the order of combining the reactants. Knowing k_2 and k_2k_3, we can obtain

$$k_3 = (5.5 \pm 0.3) \times 10^7 (\text{l mol}^{-1}\text{ s}^{-1})^2.$$

Unfortunately, it seems impossible to estimate k_6 from the $k^{term}_{Ar(OH)O^{\cdot}}$ value obtained and from the calculated rate constants k_2, k_3, k_V, and k_4 because of the large error in the resulting estimate. We determined k_6 by a new method based on the unsteady-state kinetics of the initiated reaction between QDI and $Ar(OH)_2$ [11]. For this purpose, an $Ar(OH)_2$ solution with the initiator was initially prepared in the reactor. This solution was held for 7–10 min under bubbling argon (Fig. 2). Thereafter, we added QDI, and, after 20 s, began to record the QDI disappearance kinetics. The k_6 value was derived from the dependence of the decrement of the quinoneimine concentration in a given short time (t = 20 s) from the onset of the reaction upon the addition of QDI (unsteady-state stage of the reaction) on the initiation rate:

$$\ln\frac{[QDI]_0}{[QDI]_t} = -k_2[Ar(OH)O^{\cdot}]_{st}t + \frac{k_2}{2k^{term}_{Ar(OH)O^{\cdot}}}\ln\frac{([Ar(OH)O^{\cdot}]_0 + [Ar(OH)O^{\cdot}]_{st})e^{4k^{term}_{Ar(OH)O^{\cdot}}[Ar(OH)O^{\cdot}]_{st}t} - ([Ar(OH)O^{\cdot}]_0 - [Ar(OH)O^{\cdot}]_{st})}{2[Ar(OH)O^{\cdot}]_{st}}, \quad (16)$$

where $[Ar(OH)O^{\cdot}]_0 = (w_i/(2k_6))^{1/2}$ and $[Ar(OH)O^{\cdot}]_{st} = (w_i/(2k^{term}_{Ar(OH)O^{\cdot}}))^{1/2}$.

By fitting the data of two series of experiments to formula (16), we determined the rate constant of the disproportionation of the 2,5-dichlorosemiquinone radical: $k_6 = (3.0 \pm 0.5) \times 10^6$ l mol^{-1} s^{-1}.

The disproportionation rate constants of structurally similar semiquinone radicals [27–29] are larger than this k_6 value by one order of magnitude or more. This large difference is likely due to the solvent effect on the rate constants of these reactions. Nearly all of the data reported in [27–29] were obtained in polar solvents (water–alcohol mixtures, acetonitrile), while our k_6 value pertains to the reaction in chlorobenzene.

The rate constants of reverse reactions (–2), (–3,), (–4), and (–6) were determined by experiments in which the products were added to the reaction system. The addition of H_2QDI makes significant the contribution from reactions (–3) and (–4). In this case, based on the above scheme, we arrive at the following expression for w_{QDI} [30]:

$$w_{QDI} = \left(\frac{k_2^2k_3^2[Ar(OH)_2]^2[QDI]^3 \times (k_1[Ar(OH)_2] + k_{-4}[H_2QDI])}{k_4(k_2[QDI] + k_{-3}[H_2QDI])^2 + k_3k_V[Ar(OH)_2](k_2[QDI] + k_{-3}[H_2QDI]) + k_6k_3^2[Ar(OH)_2]^2}\right)^{1/2}. \quad (17)$$

In the presence of Q added, it is necessary to take into consideration reactions (–2) and (–6):

$$w_{QDI} = \left(\frac{k_2^2k_3^2[Ar(OH)_2]^3[QDI]^2 \times (k_1[QDI] + k_{-6}[Q])}{k_4k_2^2[QDI]^2 + k_Vk_2[QDI](k_{-2}[Q] + k_3[Ar(OH)_2]) + k_6(k_{-2}[Q] + k_3[Ar(OH)_2])^2}\right)^{1/2}. \quad (18)$$

The concentrations of all compounds appearing in Eqs. (17) and (18) refer to the inflection point of the QDI consumption curve, and they should be calculated using the $[QDI]_{infl}$ values determined via formula (3) with the stoichiometry of the reaction taken into account. The dependences of w_{QDI} on the addition concentrations $[H_2QDI]_{infl}$ and $[Q]_{infl}$ in a series of runs with preset initial reactant concentrations $[QDI]_0$ and $[Ar(OH)_2]_0$ are shown in Figs. 7 and 8. The points in Figs. 7 and 8 represent the experimental data that were fitted to formula (17) or (18) by iterative methods for calculating the rate constants k_{-2}, k_{-3}, k_{-4}, and k_{-6} (Table 2).

According to Eqs. (17) and (18), the reaction rates at the w_{QDI} inflection point at equal concentrations of the three compounds are proportional to the squared concentration. For example, it follows from Eq. (17) that, at $[QDI]_{infl} = [Ar(OH)_2]_{infl} = [H_2QDI]_{infl}$,

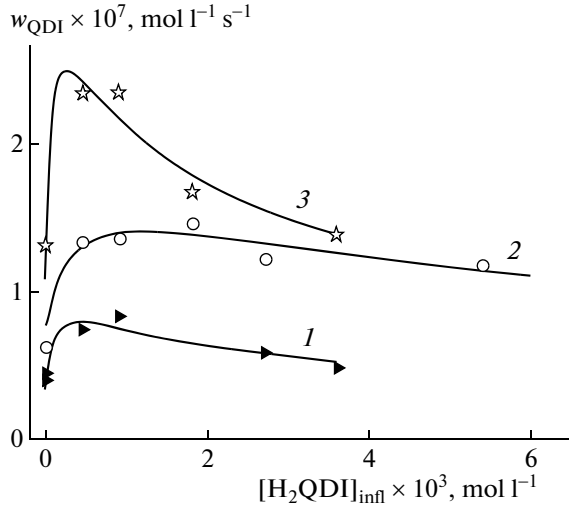


Fig. 7. w_{QDI} as function of the *N*,*N*'-diphenyl-1,4-phenylenediamine concentration $[H_2QDI]_{infl}$. The initial reactant concentrations ($\times 10^4$, mol/l) are invariable in each particular experimental series: (*1*) $[QDI]_0 = [Ar(OH)_2]_0 = 0.90$; (*2*) $[QDI]_0 = 0.90$, $[Ar(OH)_2]_0 = 1.80$; (*3*) $[QDI]_0 = [Ar(OH)_2]_0 = 1.80$. The points represent experimental data, and the lines represent the iterative calculation via formula (17) at series-average $[QDI]_{infl}$ and $[Ar(OH)_2]_{infl}$ values ($\times 10^4$, mol/l) of (*1*) 0.82, 0.82; (*2*) 1.74, 0.84; (*3*) 1.45, 1.45. Chlorobenzene, 298 K, bubbling argon.

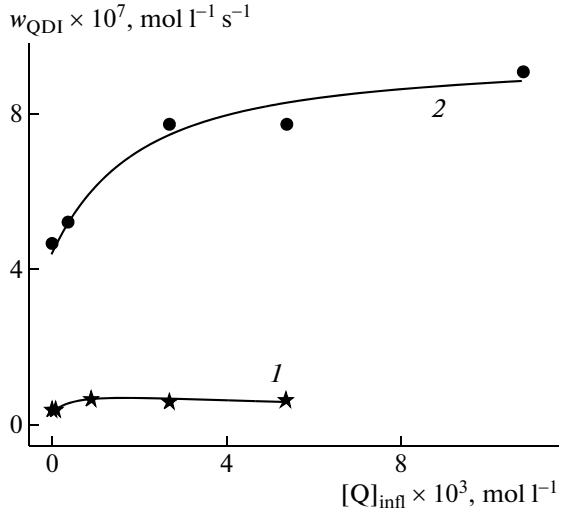


Fig. 8. w_{QDI} as a function of the 2,5-dichloroquinone concentration $[Q]_{infl}$. The initial reactant concentrations ($\times 10^4$, mol/l) are invariable in each particular experimental series: (*1*) $[QDI]_0 = [Ar(OH)_2]_0 = 0.90$; (*2*) $[QDI]_0 = [Ar(OH)_2]_0 = 3.60$. The points represent experimental data, and the lines represent the iterative calculation via formula (18) at series-average $[QDI]_{infl}$ and $[Ar(OH)_2]_{infl}$ values ($\times 10^4$, mol/l) of (*1*) 0.78, 0.78 and (*2*) 2.94, 2.94. Chlorobenzene, 298 K, bubbling argon.

$$w_{QDI} = k_2 k_3 \left(\frac{k_1 + k_{-4}}{k_4 (k_2 + k_{-3})^2 + k_3 k_V (k_2 + k_{-3}) + k_6 k_3^2} \right)^{1/2} \times [QDI]^2 = \alpha [QDI]_{infl}^2 . \quad (19)$$

From Eq. (18) at $[QDI]_{infl} = [Ar(OH)_2]_{infl} = [Q]_{infl}$, it follows that

$$w_{QDI} = k_2 k_3 \left(\frac{k_1 + k_{-6}}{k_4 k_2^2 + k_2 k_V (k_{-2} + k_3) + k_6 (k_{-2} + k_3)^2} \right)^{1/2} \times [QDI]^2 = \beta [QDI]_{infl}^2 . \quad (20)$$

Experimental verification of expressions (19) and (20) meets difficulties because it is difficult to establish equivalent concentrations of the initial compounds and reaction products at the inflection point of the QDI disappearance curve. However, the results of experiments at equal initial concentrations lead to quite reliable semiquantitative conclusions. Figure 4 presents experimental data obtained at $[QDI]_0 = [Ar(OH)_2]_0 = [H_2QDI]_0$ (line *2*) and at $[QDI]_0 = [Ar(OH)_2]_0 = [Q]_0$ (line *3*). In both cases, $[QDI]_{infl}$ calculated via formula (3) was used as the compound concentrations at the inflection point. From the slopes of the lines plotted in Fig. 4, we determine the following quantities (l mol^{-1} s^{-1}):

$$\alpha_{exp} = 6.85 \pm 0.58, \quad \beta_{exp} = 6.35 \pm 0.24.$$

By substituting the rate constants determined in this work into Eqs. (19) and (20) (without errors taken into account), we obtain

$$\alpha_{calc} = 7.09, \quad \beta_{calc} = 6.04.$$

Table 2. Rate constants of reverse steps obtained by fitting experimental w_{QDI} data as a function of the added product concentration to formulas (17) and (18)

Curve number	$k_{-3} \times 10^{-5}$	$k_{-4} \times 10^4$	$k_{-2} \times 10^{-6}$	$k_{-6} \times 10^5$
	l mol^{-1} s^{-1}			
1, Fig. 7	7.5 ± 4.5	1.8 ± 1.3	–	–
2, Fig. 7	9.5 ± 1.4	1.2 ± 0.2	–	–
3, Fig. 7	9.2 ± 2.9	2.1 ± 0.7	–	–
1, Fig. 8	–	–	4.5 ± 2.5	8.9 ± 6.1
2, Fig. 8	–	–	8.9 ± 7.2	6.0 ± 3.9
Average	8.7 ± 2.8	1.7 ± 1.1	6.7 ± 4.7	7.5 ± 4.3

Clearly, the experimental and calculated data are in satisfactory agreement in spite of the error in the $[QDI]_{infl}$ values used in the determination of α_{exp} and β_{exp} from the data presented in Fig. 4 and in spite of the estimating character of the calculation of α_{calc} and β_{calc}.

Thus, using the reversible chain reaction between *N*,*N*'-diphenyl-1,4-benzoquinonediimine and 2,5-dichlorohydroquinone as an example, we have described a new approach to determination of the rate constant of elementary steps for chain reactions having a self-acceleration period due to the long time necessary for the reaction to come to the steady state. The empirical function $y = a\exp(bt^c) + d$ is suggested for approximating the S-shaped kinetic curves. This function provides a good fit to experimental data up to a large extent of the reaction. The kinetic parameters of the reaction (initial quinoneimine concentration, reaction rate, induction period, calculated rate constants) depend strongly on the experimental procedure, including the order in which the reactants and initiator are introduced into the system and the reactor charging time.

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