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Kinetics and Mechanism of the Chain Reaction of *N*-Phenyl-1,4-Benzoquinone Monoimine with 2,5-Dimethylhydroquinone

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Abstract—The kinetics of the reaction of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-dimethyl-1,4-hydroquinone in chlorobenzene was studied at 298.2 and 340 K. The reaction occurs by a chain mechanism with a chain length of $\sim 10^2$–10^3 units, depending on temperature and reactant concentrations. The orders of reaction with respect to components and the rate constants (or estimated values) were determined for all of the elementary steps at 298.2 and 340 K. The experimental data were compared with the results obtained previously for the reaction of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-di-*tert*-butyl-1,4-hydroquinone. The nature of substituents in hydroquinone exerts a strong effect on the kinetic parameters of this new class of chain reactions. The effect of the final product, 2,5-dimethylquinone, on the reaction kinetics at 298.2 and 340 K was studied, and it was found that 2,5-dimethylquinone additives has only a weak inhibiting effect. The rate constant of the reaction of 2,5-dimethylquinone with semiquinone radicals, which were produced from 4-hydroxydiphenylamine, was estimated: $k_{-2} \sim 10^4$–10^5 l mol^{-1} s^{-1}.

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INTRODUCTION

Benzoquinone imines are nitrogen analogs of quinones. In this context, the reactions of benzoquinone imines with hydroquinones can be assigned to a broader class of quinone reactions with valence-saturated compounds. These reactions result in the reduction of quinones to hydroxyphenoxy (semiquinone) radicals and then to hydroquinones. The mechanism of radical reactions with the participation of quinone compounds is of considerable interest in chemistry and biology. For example, these compounds are used as radical polymerization inhibitors [1–3]. They are formed from phenol and aromatic amine antioxidants under conditions of oxidation inhibited by these antioxidants, and they have a significant effect on the overall inhibitor efficiency [4–6]. On the other hand, the reactions of H-atom abstraction by quinones play a key role in the mechanism of the protective action of bioantioxidants from the class of quinones (ubiquinones and vitamin K group) [7].

In the past few years [8, 9], with the use of a reaction of *N*-phenyl-1,4-benzoquinone monoimine (QMI) with 2,5-di-*tert*-butyl-1,4-hydroquinone in chlorobenzene as an example, it was found that quinone imines react with hydroquinones by a radical chain mechanism. Experiments performed in the presence of 4-hydroxydiphenylamine, which was a reaction product, demonstrated a pronounced reversible character of chain propagation and termination steps [9, 10]. Experiments with the addition of the second final product, 2,5-di-*tert*-butylquinone, were not performed, and the question of the reversibility of analogous steps with the participation of quinone is still an open question.

Considering an important role of radical reactions with the participation of quinones and taking into account the unique mechanism of chain reactions between quinone imines and hydroquinones (very long chains and the pronounced reversibility of elementary steps with the participation of quinone imine and its reduced species), we studied the reaction of QMI with 2,5-dimethylhydroquinone ($Ar(OH)_2$), which is a close analog of 2,5-di-*tert*-butylhydroquinone. Preliminary data on the reaction kinetics at 298 K were briefly reported previously [11]. In this work, we extended the range of experimental data and studied the effects of temperature and 2,5-dimethylquinone (Q) on the reaction kinetics.

EXPERIMENTAL

The procedures used for the synthesis and purification of QMI and the solvent (chlorobenzene) were described previously [9]. 2,5-Dimethyl-1,4-hydroquinone, which was synthesized according to a published procedure [12], was kindly provided by I.K. Yakushchenko. The additional purification of $Ar(OH)_2$ was performed by liquid chromatography on SiO_2 with the use of an ethyl acetate–benzene mixture as the eluent. The reaction kinetics was studied at 298.2 ± 0.1 and 340.0 ± 0.5 K in a thermostated bubbling-type quartz reactor cell (volume of 8.5 ml; optical path length $l = 2.0$ cm; argon bubbling) embedded in a Specord UV–VIS spectrophotometer. The true reactant concentrations at 340 K were calculated with consideration for the thermal expansion of chlorobenzene (1×10^{-3} K^{-1}). In the course of experiments, the quinone imine absorbance was continuously measured at ν = const = 22260, 20000, or 19000 cm^{-1} depending on the initial concentration of QMI. The resulting 2,5-dimethyl-1,4-quinone also absorbs in this region, but its absorption can be ignored because of a low molar extinction coefficient ($\varepsilon_{22260} = 21$ l mol^{-1} cm^{-1}).

The kinetics of the reaction of QMI with Ar(OH)$_2$ was quantitatively studied using the initial rates (w_{QMI}) of quinone imine consumption, when the effect of products, which may complicate the kinetics, can be ignored. In order to determine the numerical values of w_{QMI}, the experimental curves of the decrease in absorbance A with time t were treated using the empirical equation

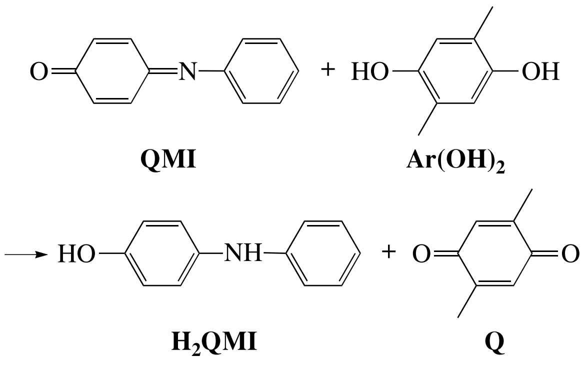
$$\ln\{b + \ln(A - a)\} = c + dt,$$

where a, b, c, and d are parameters chosen by an iteration method. The absorbance A_0 at $t = 0$ was calculated based on the found values of these parameters; thereafter, w_{QMI} was found from the equation

$$w_{\mathrm{QMI}} = -d(A_0 - a)\{b + \ln(A_0 - a)\}/(\varepsilon l).$$

RESULTS AND DISCUSSION

At concentrations of 10^{-4}–10^{-3} mol/l, the reaction of QMI with Ar(OH)$_2$ was complete in a matter of minutes; it proceeded until almost complete consumption of the deficient component. In the course of the reaction, QMI was reduced to 4-hydroxydiphenylamine (H$_2$QMI), whereas Ar(OH)$_2$ was oxidized to Q. The formation of these products was verified by liquid chromatography.



The reaction has a complex mechanism, as evidenced by the fractional orders $n_{\mathrm{Ar(OH)_2}}$ and n_{QMI} with respect to the reactants. Data shown in Fig. 1 suggest that $n_{\mathrm{Ar(OH)_2}} = 1.1$–$1.35$ and $n_{\mathrm{QMI}} = 0.65$–0.85, regardless of temperature and reactant concentrations.

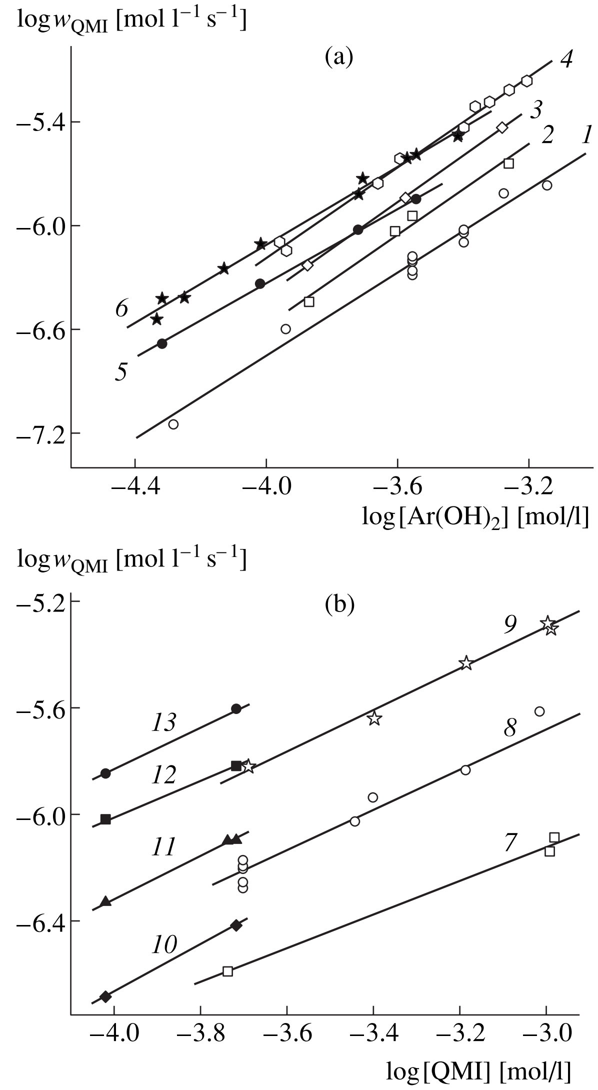


Fig. 1. Determination of the orders of reaction (a) $n_{\mathrm{Ar(OH)_2}}$ and (b) n_{QMI} from the dependence of w_{QMI} on reactant concentrations. (a) $[\mathrm{QMI}]_0 \times 10^4$ = (*1*) 2.0, (*2*) 4.0, (*3*) 6.5, (*4*) 10.0, (*5*) 0.975, and (*6*) 1.9 mol/l. (b) $[\mathrm{Ar(OH)_2}]_0 \times 10^4$ = (*7*) 1.15, (*8*) 2.6, (*9*) 4.9, (*10*) 0.478, (*11*) 0.957, (*12*) 1.91, and (*13*) 2.87 mol/l. T = (*1–4*, *7–9*) 298.2 or (*5*, *6*, *10–13*) 340.0 K.

The chain mechanism was demonstrated experimentally in the presence of an initiator, tetraphenylhydrazine (TPH, Ph$_2$N–NPh$_2$), which decomposes into diphenylaminyl radicals Ph$_2$N$^{\bullet}$ on heating. These radicals very actively ($k \sim 10^7$–10^8 l mol^{-1} s^{-1} [13]) react with phenols and hydroquinones to abstract H atoms from them and to be converted into phenoxy and hydroxyphenoxy (semiquinone) radicals. The rate constants k_{i} of initiation due to the degradation of TPH were calculated from the equation $k_i = 2ek_{\text{deg}}^{\text{TPH}} = 1.90k_{\text{deg}}^{\text{TPH}}$, where $e = 0.950 \pm 0.015$ is the probability of radical escape into the bulk, and $k_{\text{deg}}^{\text{TPH}} = 10^{13.89}\exp(-117500/RT)$ s^{-1} [9]. At 298.2 and 340.0 K, $k_i = 3.91 \times 10^{-7}$ and 1.31×10^{-4} s^{-1}, respectively. As can be seen in Fig. 2, the rate of reaction increases in the presence of the initiator, and a linear relation between w_i and w_{QMI}^2 took place. This fact suggests that the reaction occurs via a chain mechanism, and it is characterized by quadratic-law chain termination. The intercepts of straight lines on the axis of ordinates in Fig. 2 are positive; this indicates that the formation of radicals in the absence of an initiator occurs due to intrinsic processes in the QMI + Ar(OH)$_2$ system. The chain length can be roughly estimated from data in Fig. 2: thus, at $T = 298.2$ K, an increase in w_i by ~10^{-9} mol l^{-1} s^{-1} caused an increase in w_{QMI} by ~10^{-7} mol l^{-1} s^{-1}. Hence, it follows that the chain length is $\nu = \Delta w_{\text{QMI}}/\Delta w_i \sim 10^2$ units.

The reaction of QMI with Ar(OH)$_2$ occurs via a mechanism analogous to that proposed for the reaction of QMI with 2,5-di-*tert*-butyl-1,4-hydroquinone [8]. This mechanism involves the following elementary steps:

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

$$\text{QMI} + \text{Ar(OH)}_2 \longrightarrow \text{HQMI}^\bullet + \text{Ar(OH)O}^\bullet \qquad \text{chain initiation} \qquad (1)$$

$$\text{QMI} + \text{Ar(OH)O}^\bullet \longrightarrow \text{HQMI}^\bullet + \text{Q} \qquad \text{chain propagation} \qquad (2)$$

$$\text{HQMI}^\bullet + \text{Ar(OH)}_2 \longrightarrow \text{H}_2\text{QMI} + \text{Ar(OH)O}^\bullet \qquad \text{—''—} \qquad (3)$$

$$\text{HQMI}^\bullet + \text{HQMI}^\bullet \longrightarrow \text{H}_2\text{QMI} + \text{QMI} \qquad \text{chain termination} \qquad (4)$$

$$\text{HQMI}^\bullet + \text{Ar(OH)O}^\bullet \longrightarrow \text{H}_2\text{QMI} + \text{Q}\ (\text{QMI} + \text{Ar(OH)}_2) \qquad \text{—''—} \qquad (5)$$

$$\text{Ar(OH)O}^\bullet + \text{Ar(OH)O}^\bullet \longrightarrow \text{Ar(OH)}_2 + \text{Q} \qquad \text{—''—} \qquad (6)$$

The above reaction scheme reflects the mechanism in the simplest form. Here, HQMI$^\bullet$ denotes radicals that are formed by the addition (or abstraction) of an H atom to the QMI molecule (or from the H$_2$QMI molecule). These can be either 4-hydroxydiphenylaminyl (HO–C$_6$H$_4$–N$^\bullet$–C$_6$H$_5$) or 4-anilinophenoxy ($^\bullet$O–C$_6$H$_4$–NH–C$_6$H$_5$) radicals. For simplicity, they are considered indistinguishable; that is, the same reactivity of these radicals in reactions of the same type is assumed.

In order to obtain an expression for the rate of reaction, let us use the equation for long chains, which is obeyed with a high degree of accuracy at $\nu \sim 10^2$:

$$\begin{aligned} w_{\text{QMI}} &= k_2[\text{QMI}][\text{Ar(OH)O}^\bullet] \\ &= k_3[\text{HQMI}^\bullet][\text{Ar(OH)}_2]. \end{aligned} \qquad \text{(I)}$$

From Eq. (I), we can express the concentrations of HQMI$^\bullet$ and Ar(OH)O$^\bullet$ radicals in terms of w_{QMI}:

$$\begin{aligned} [\text{Ar(OH)O}^\bullet] &= \frac{w_{\text{QMI}}}{k_2[\text{QMI}]}, \\ [\text{HQMI}^\bullet] &= \frac{w_{\text{QMI}}}{k_3[\text{Ar(OH)}_2]}. \end{aligned} \qquad \text{(II)}$$

Substituting (II) into the steady-state equation

$$\begin{aligned} &k_1[\text{QMI}][\text{Ar(OH)}_2] + 0.5w_i \\ &= k_4[\text{HQMI}^\bullet]^2 + k_5[\text{HQMI}^\bullet][\text{Ar(OH)O}^\bullet] \\ &\quad + k_6[\text{Ar(OH)O}^\bullet]^2, \end{aligned} \qquad \text{(III)}$$

we obtain the following expression for the rate of reaction:

$$w_{\text{QMI}}^2 = \frac{k_2^2k_3^2[\text{QMI}]^2[\text{Ar(OH)}_2]^2(k_1[\text{QMI}][\text{Ar(OH)}_2] + 0.5w_i)}{k_4k_2^2[\text{QMI}]^2 + k_5k_2k_3[\text{Ar(OH)}_2][\text{QMI}] + k_6k_3^2[\text{Ar(OH)}_2]^2}. \qquad \text{(IV)}$$

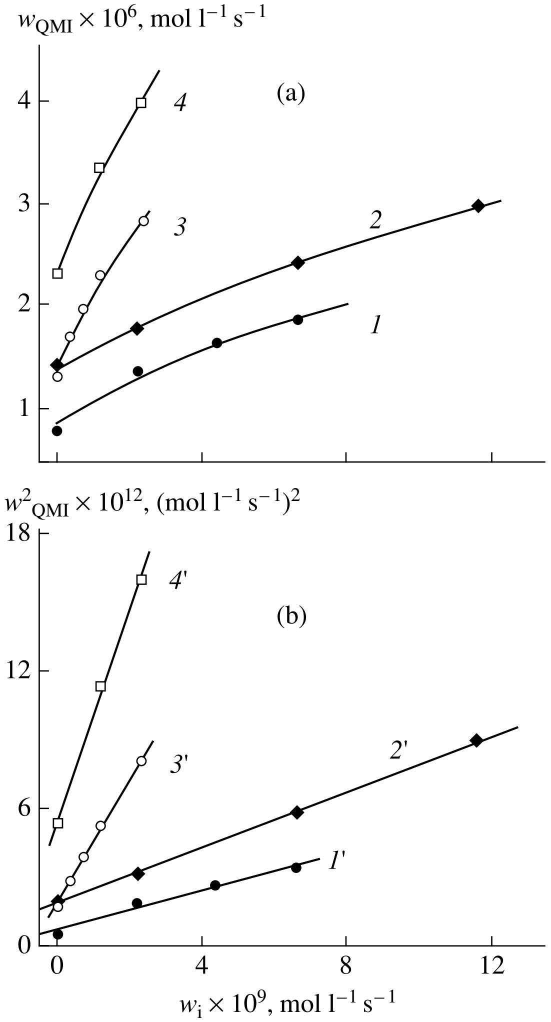


Fig. 2. (a) (*1–4*) Dependence of the initial rate of reaction (w_{QMI}) on the rate of initiation and (b) (*1'–4'*) the treatment of curves *1–4* in the w^2_{QMI}–w_i coordinates. QMI and $Ar(OH)_2$ concentrations ×10^4 (mol/l), respectively: (*1*, *1'*) 1.87 and 0.957, (*2*, *2'*) 0.90 and 2.87, (*3*, *3'*) 3.7 and 2.6, or (*4*, *4'*) 3.7 and 5.5. T = (*1*, *2*, *1'*, *2'*) 340.0 or (*3*, *4*, *3'*, *4'*) 298.2 K.

At $w_i = 0$, Eq. (IV) can be written as follows:

$$\left(\frac{[QMI][Ar(OH)_2]}{w_{QMI}}\right)^2 = \frac{k_5}{k_1k_2k_3} + \frac{k_4}{k_1k_3^2}\frac{[QMI]}{[Ar(OH)_2]} + \frac{k_6}{k_1k_2^2}\frac{[Ar(OH)_2]}{[QMI]}. \quad \text{(V)}$$

Let us denote the left-hand side of Eq. (V) by Y and the ratio $[QMI]/[Ar(OH)_2]$ by X and write Eq. (V) in the following form:

$$Y = a + bX + c\frac{1}{X}, \quad \text{(VI)}$$

where a, b, and c are the parameters of Eq. (V).

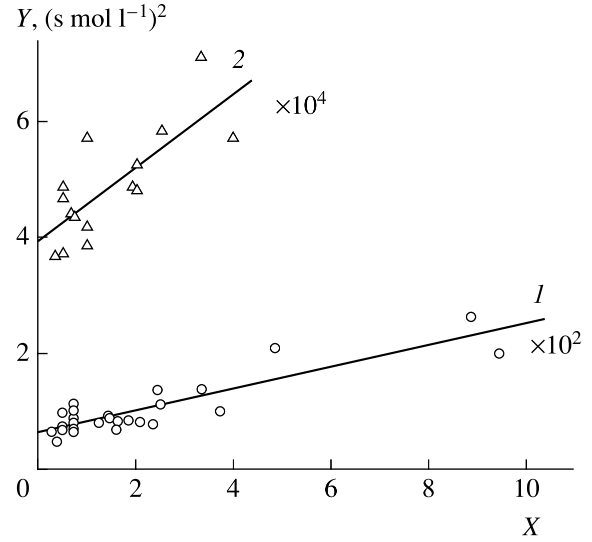


Fig. 3. Treatment of the results of experiments performed in the absence of an initiator in the X–Y coordinates of Eq. (VI). T = (*1*) 298.2 or (*2*) 340.0 K.

Figure 3 shows the results of data processing in the X–Y coordinates of Eq. (VI) in the absence of an initiator. At T = 298.2 and 340.0 K, all points lie along straight lines within the limits of experimental error. Therefore, the last term in the right-hand side of Eq. (VI) can be neglected; that is, reaction (6) of chain termination can be ignored under the experimental conditions.

The following kinetic parameters were obtained from the slopes and ordinate intercepts in Fig. 3:

Parameter	298.2 K	340.0 K
$\frac{k_5}{k_1k_2k_3}$, (mol s l^{-1})^2	$(6.5 \pm 0.6) \times 10^{-3}$	$(3.9 \pm 0.3) \times 10^{-4}$
$\frac{k_4}{k_1k_3^2}$, (mol s l^{-1})^2	$(1.9 \pm 0.19) \times 10^{-3}$	$(6.4 \pm 1.5) \times 10^{-5}$

For processing the experimental data obtained in the presence of the initiator, let us use the equation

$$\frac{[QMI] + \alpha[Ar(OH)_2]}{[QMI]^2[Ar(OH)_2]^3}w^2_{QMI} = \frac{k_1k_3^2}{k_4} + \frac{0.5k_3^2w_i}{k_4[QMI][Ar(OH)_2]} \quad \text{(VII)}$$

or

$$Z = \frac{k_1k_3^2}{k_4} + 0.5\frac{k_3^2}{k_4}U, \quad \text{(VIIa)}$$

which is derived from (IV) with neglect of reaction (6). Here, the parameter $\alpha = k_3k_5/(k_2k_4)$ is introduced. The

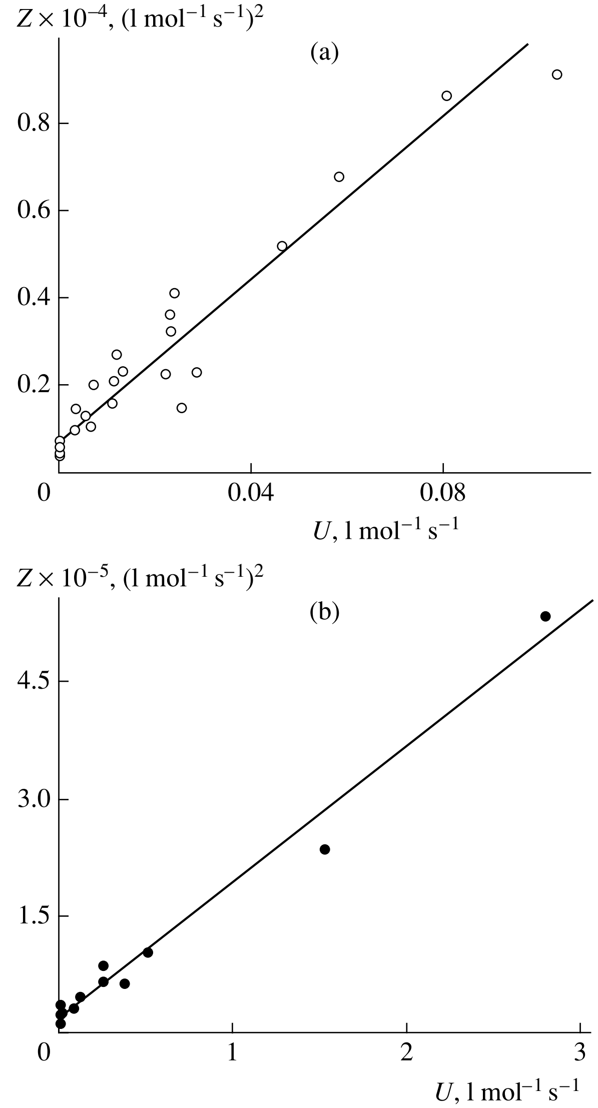


Fig. 4. Treatment of the results of experiments performed in the presence of the initiator with the use of Eq. (VIIa). T = (a) 298.2 or (b) 340.0 K.

numerical values of this parameter were obtained from the above data: $\alpha = 3.45 \pm 0.66$ at $T = 298.2$ K and $\alpha = 6.14 \pm 1.85$ at $T = 340.0$ K.

As can be seen in Fig. 4, Eq. (VIIa) is consistent with experimental data. The parameters of straight lines in Fig. 4 have the following values:

Parameter	298.2 K	340.0 K
$\frac{k_1 k_3^2}{k_4}$, $(\mathrm{l\ mol^{-1}\ s^{-1}})^2$	$(6.45 \pm 0.8) \times 10^2$	$(1.71 \pm 0.28) \times 10^4$
$0.5\frac{k_3^2}{k_4}$, $\mathrm{l\ mol^{-1}\ s^{-1}}$	$(9.5 \pm 0.3) \times 10^4$	$(1.77 \pm 0.04) \times 10^5$

Assuming that $k_4 = k_5 = 8 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$ (as in reactions of a number of other semiquinone radicals [14]), we find the absolute values of k_3 and $k_2 = k_3/\alpha$ from the above data. In this case, the rate constants can be determined or reliably estimated for all steps in the reaction mechanism (Table 1). For convenience of comparison, Table 1 also summarizes data for the reaction of QMI with 2,5-di-*tert*-butylhydroquinone.

The temperature dependence of k_1 can be written in the form (E_1, kJ/mol)

$$k_1,\ \mathrm{l\ mol^{-1}\ s^{-1}} = 8.22 \times 10^6 \exp(-53.6/RT).$$

A comparison between this expression and the expression

$$k_1,\ \mathrm{l\ mol^{-1}\ s^{-1}} = 1.27 \times 10^9 \exp(-66.2/RT),$$

which was obtained previously [9] for the reaction of QMI with 2,5-di-*tert*-butylhydroquinone, indicates that the activation energy and the preexponential factor increase symbatically; that is, it is likely that a compensation effect is characteristic of the reactions of QMI with hydroquinones. It is believed that this effect can be partially due to the difference between the solvation energies of 2,5-dimethylhydroquinone and 2,5-di-*tert*-butylhydroquinone, as well as their activated complexes with QMI in the course of the reaction.

Note that the reactions of radical formation in the interaction of quinones (quinone imines) with hydroquinones (see elementary step (1)) are very poorly known, and the values of k_1 for the above two reactions of QMI with hydroquinones remain the only reliable experimental data.[1] This work demonstrates that, in particular, the true values of k_1 can be found from the kinetics of chain reactions in quinone (quinone imine)–hydroquinone systems.

The chain mechanism explains the fractional orders of reaction with respect to the components. At $w_\mathrm{i} = 0$, excluding reaction (6) from (IV), we obtain

$$w_\mathrm{QMI} = (k_1 k_2)^{1/2} k_3 \times \frac{[\mathrm{QMI}][\mathrm{Ar(OH)_2}]^{3/2}}{(k_2 k_4[\mathrm{QMI}] + k_3 k_5[\mathrm{Ar(OH)_2}])^{1/2}}. \qquad \text{(VIII)}$$

From relation (VIII), it follows that, in the absence of an initiator, the expected values of n_QMI and $n_{\mathrm{Ar(OH)_2}}$ lie within the ranges $0.5 < n_\mathrm{QMI} < 1$ and $1 < n_{\mathrm{Ar(OH)_2}} < 1.5$, respectively. The above experimental data are consistent with this conclusion.

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[1] The dehydrogenation reactions of organic compounds under the action of quinones (quinone imines) have been studied for a long time; reaction rate constants obtained without considering a chain mechanism have been reported [15–19]. As can be seen, in the case of reactions with hydroquinones, these data should be considered tentative because the true values of the rate constants k_1 of elementary reactions (1) are really smaller by a factor of ν.

Table 1. Rate constants of the elementary steps of the chain reactions of *N*-phenyl-1,4-benzoquinone monoimine (QMI) with 2,5-dimethylhydroquinone ($Ar(OH)_2$) and 2,5-di-*tert*-butylhydroquinone [9] (in parentheses) in chlorobenzene

Step	Reaction	k, l mol^{-1} s^{-1}	
		298.2 K	340.0 K
(1)	$QMI + Ar(OH)_2 \longrightarrow HQMI^\bullet + Ar(OH)O^\bullet$	$(3.4 \pm 0.5) \times 10^{-3}$ $((3.2 \pm 0.2) \times 10^{-3})$	$(4.8 \pm 0.9) \times 10^{-2}$ $((8.6 \pm 0.5) \times 10^{-2})$
(2)	$QMI + Ar(OH)O^\bullet \longrightarrow HQMI^\bullet + Q$	3.56×10^6 (3.47×10^7)	2.74×10^6 (1.28×10^7)
(3)	$HQMI^\bullet + Ar(OH)_2 \longrightarrow H_2QMI + Ar(OH)O^\bullet$	1.23×10^7 (1.65×10^7)	1.68×10^7 (1.75×10^7)
(4)	$HQMI^\bullet + HQMI^\bullet \longrightarrow H_2QMI + QMI$	8×10^8*	8×10^8*
(5)	$HQMI^\bullet + Ar(OH)O^\bullet \longrightarrow H_2QMI + Q$ $(QMI + Ar(OH)_2)$	8×10^8*	8×10^8*

* By hypothesis.

The reaction chain length (ν) can be calculated as the average number of QMI molecules reduced to H_2QMI per radical formed:

$$\nu = \frac{w_{QMI}}{w_{i,\Sigma}} = \frac{k_3[Ar(OH)_2]}{2(k_1[QMI][Ar(OH)_2] + 0.5w_i)^{1/2}} \times \left(\frac{k_2[QMI]}{k_2k_4[QMI] + k_3k_5[Ar(OH)_2]}\right)^{1/2}, \quad (IX)$$

where $w_{i,\Sigma}$ is the overall rate of radical formation in the system. Table 2 summarizes the values of ν. It can be seen that, in the absence of an initiator, the chain length varies from 10^2 to 10^3 units, depending on reactant concentrations and temperature. In the presence of the initiator, ν decreases.

Previously, we studied the effect of a final product, 4-hydroxydiphenylamine (H_2QMI), on the chain reaction of QMI with 2,5-di-*tert*-butylhydroquinone. We found that, in the presence of small H_2QMI additives (~10^{-4} mol/l), the rate of reaction significantly (several times) increased; however, the rate decreased at higher concentrations of H_2QMI. In general, the dependence of w_{QMI} on $[H_2QMI]_0$ had the shape of a curve with a maximum [9, 10]. The complex character of the above dependence was quantitatively described based on the assumption that reverse elementary reactions (–3) and (–4) occurred in the presence of H_2QMI in the system. Considering the above mechanism of the chain reaction of QMI with $Ar(OH)_2$, we can notice that initiation step (1) and chain-termination step (5) are also forward and reverse elementary reactions with respect to each other. Thus, if the well-defined reversible character of the other two elementary reactions (–2) and (–6) is demonstrated experimentally, the overall chain reaction of QMI with $Ar(OH)_2$ can be considered as a reversible chain reaction.

When discussing the reversibility of chain reactions in quinone imine + hydroquinone systems, we keep in mind the following: In the course of the above reactions, two parent substances are quantitatively converted into two reaction products:

$$QMI + Ar(OH)_2 \longleftrightarrow H_2QMI + Q. \quad (s, -s)$$

Thermodynamically, reaction (s) leads the system to an equilibrium state, which is characterized by a certain equilibrium constant (K_s) at temperature T. Let us tentatively consider that this reaction is irreversible if $K_s \gg 1$. For reactions with a pronounced reversible character, the equilibrium constant is close to unity ($K_s \sim 1$). If forward reaction (s) and really occurring reverse reaction (–s) proceed via the same chain mechanism; that is, if the equilibrium state can be reached from the sides of both parent substances and products, we consider this reaction a reversible chain reaction. Indeed, recently [20], we found such a reaction in the QMI + 2.5-dichlorohydroquinone system; $K_s = 0.38$ at 298.2 K.

We can demonstrate that $K_s = K_2K_3$ at long chains [21]. As a first approximation, we can ignore entropy changes in overall reaction (s) and at chain-propagation steps (2) and (3) and consider that $\Delta H \approx \Delta G = -RT\ln K_s = -RT\ln K_2 + -RT\ln K_3$. The chain length of forward reaction increases with k_2 and k_3, whereas the chain length of reverse reaction increases with k_{-2} and k_{-3}. Hence, it can be seen that the pronounced reversible character of complex chain reaction (s) can be expected at a pronounced reversible character of single-step elementary chain-propagation reactions, that is, in

Table 2. Effects of the reactant and initiator concentrations and temperature on the initial rate of reaction (w_{QMI}) and on the chain length (ν)

$[\mathrm{QMI}]_0 \times 10^4$, mol/l	$[\mathrm{Ar(OH)_2}]_0 \times 10^4$, mol/l	$w_{\mathrm{i}} \times 10^9$, mol l^{-1} s^{-1}	$w_{\mathrm{QMI}} \times 10^6$, mol l^{-1} s^{-1}	$(w_{\mathrm{QMI}})^*_{\mathrm{calcd}} \times 10^6$, mol l^{-1} s^{-1}	$\nu^{**}_{\mathrm{expt}} \times 10^{-3}$	$\nu^{***}_{\mathrm{calcd}} \times 10^{-3}$
298.2 K						
2.01	0.52	0	0.071	0.098	1.01	1.38
1.84	1.15	0	0.26	0.24	1.79	1.66
2.00	4.0	0	0.80	1.02	1.48	1.88
2.00	4.0	0	0.92	1.02	1.70	1.88
2.05	5.3	0	1.54	1.40	2.09	1.91
1.95	7.21	0	1.73	1.84	1.81	1.94
10.4	1.10	0	0.81	0.81	1.04	1.04
10.2	2.20	0	1.78	2.00	1.17	1.31
9.59	4.0	0	3.74	4.01	1.44	1.54
10.2	6.2	0	6.88	7.09	1.60	1.65
3.65	5.50	0	2.31	2.50	1.70	1.84
3.63	5.50	1.14	3.35	3.38	1.35	1.36
3.65	5.50	2.29	3.98	4.08	1.09	1.12
340.0 K						
1.91	0.479	0	0.38	0.38	0.433	0.425
1.83	0.957	0	0.79	0.81	0.469	0.476
1.96	1.97	0	1.89	1.89	0.507	0.506
1.91	3.83	0	3.32	3.71	0.470	0.525
1.92	3.86	0	3.43	3.76	0.479	0.525
1.83	0.957	0	0.79	0.81	0.469	0.476
1.87	0.957	2.21	1.37	1.24	0.347	0.315
1.87	0.957	4.41	1.64	1.55	0.267	0.252
1.87	0.957	6.63	1.86	1.81	0.222	0.216

Note: Chlorobenzene; Ar bubbling.

* Calculated from Eq. (IV).

** $\nu_{\mathrm{expt}} = \dfrac{w_{\mathrm{QMI}}}{2k_1[\mathrm{QMI}]_0[\mathrm{Ar(OH)_2}]_0 + w_{\mathrm{i}}}$.

*** Calculated from Eq. (IX).

the case of $K_s \approx K_2 \approx K_3 \sim 1$ when reaction (s) and steps (2) and (3) are nearly thermally neutral.

In this work, we studied the effect of 2,5-dimethylquinone additives on the kinetics of the reaction of QMI with $\mathrm{Ar(OH)_2}$. We believed that, analogously to $\mathrm{H_2QMI}$, the additives of Q also have a dual effect on w_{QMI}. Indeed, it is likely that, in the presence of Q, both initiation reaction (–6) (reaction acceleration) and reaction (–2), which is the reverse of chain-propagation step (2), occur in the system from the outset to decrease the chain length and, consequently, to inhibit the reaction. The expression for the rate of reaction in the presence of Q can be obtained based on the above kinetic scheme supplemented with steps (–2) and (–6):

$$w_{\mathrm{QMI}}^2 = \frac{k_2^2 k_3^2[\mathrm{QMI}]^2[\mathrm{Ar(OH)_2}]^3(k_1[\mathrm{QMI}] + k_{-6}[\mathrm{Q}])}{k_4 k_2^2[\mathrm{QMI}]^2 + k_5 k_2[\mathrm{QMI}](k_3\mathrm{Ar(OH)_2} + k_{-2}[\mathrm{Q}])}. \quad \text{(X)}$$

In Eq. (X), terms containing [Q] occur in both the numerator and the denominator. It can be seen that, generally, the dependence of w_{QMI} on $[\mathrm{Q}]_0$ is complicated at $[\mathrm{QMI}]_0$ and $[\mathrm{Ar(OH)_2}]_0$ = const, and its form depends on the absolute values of k_{-2} and k_{-6}.

As can be seen in Fig. 5, in all of the experiments, 2,5-dimethylquinone had only a weak inhibiting effect on the reaction regardless of the temperature and QMI and $Ar(OH)_2$ concentrations. A very small effect of Q did not allow us to obtain correct estimates of the two rate constants k_{-2} and k_{-6} (it is likely that these values differ by 8–9 orders of magnitude) simultaneously by the treatment of experimental data using Eq. (X). Nevertheless, the estimated values of k_{-2} (lower estimates of k_{-2}), which can be obtained using iteration methods in the treatment of experimental data by Eq. (X) on the assumption that $k_{-6} = 0$, are of interest:

Temperature, K	Curve number in Fig. 5	$k_{-2} \times 10^{-5}$, $l\ mol^{-1}\ s^{-1}$
298.2	*1*	1.60
	2	3.70
	3	4.09
340.0	*4*	1.45
	5	0.79

It can be seen that $k_{-2} \sim 10^4$–$10^5\ l\ mol^{-1}\ s^{-1}$, which is indicative of a high activity of quinones in H-atom abstraction from semiquinone radicals. The high values of k_{-2} suggest the intense occurrence of reaction (–2) under the experimental conditions, especially, at deep steps when the system approached an equilibrium.

It can be seen in Table 1 that $k_2 \approx 3 \times 10^6\ l\ mol^{-1}\ s^{-1}$ over the temperature range chosen. Consequently, $K_2 \sim 10^{1.5}$–10^2. As an estimate of K_3, the value $K_3 \approx 5$, which was found previously [9] for a similar chain reaction of QMI with 2,5-di-*tert*-butylhydroquinone, can be used. In this case, $K_s = K_2K_3 \sim 10^2 \gg 1$. By this is meant that the reversible character of the test chain reaction is expressed only slightly.

Thus, we have studied a new chain reaction of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-dimethylhydroquinone. This reaction occurs by a mechanism analogous to that proposed previously for the reaction of QMI with 2,5-di-*tert*-butylhydroquinone. The kinetic characteristics of the two test reactions were noticeably different in spite of the similar nature of methyl and *tert*-butyl substituents and the identical positions of the substituents in the benzene rings of the hydroquinones. Thus, the rate constants of elementary steps (1) and (3) are close to each other in both of the reactions, whereas the rate constants of step (2) differ by almost one order of magnitude. Therefore, the kinetics of chain reactions between quinone imines and hydroquinones can be used as a sensitive method for studying the effect of the nature of substituents on the reactivity of hydroquinones and their semiquinone radicals as H-atom donors. In this work, we studied for the first time the effect of a final product, 2,5-dimethylquinone, on the kinetics of the reaction of $Ar(OH)_2$ with QMI and found an inhibiting effect of this product, which was explained by the reversibility of the elementary steps of formation of quinone Q. Although the additives of Q have a weak effect, we managed to roughly estimate the rate constant of elementary step (–2) from the experimental data: $k_{-2} \sim 10^4$–$10^5\ l\ mol^{-1}\ s^{-1}$.

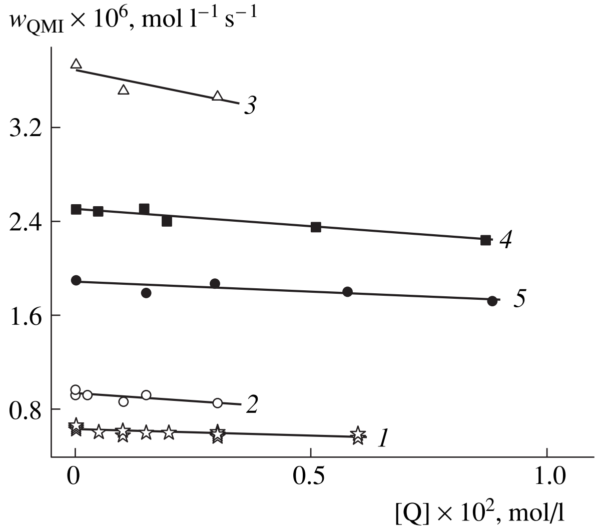

Fig. 5. Effect of 2,5-dimethylquinone (Q) on the rate of reaction (w_{QMI}). QMI and $Ar(OH)_2$ concentrations $\times 10^4$ (mol/l), respectively: (*1*) 2.0 and 2.8, (*2*) 2.0 and 4.0, (*3*) 10.0 and 4.0, (*4*) 1.92 and 2.7, or (*5*) 1.96 and 1.97. T = (*1–3*) 298.2 or (*4*, *5*) 340.0 K. Points: the experimental data. Lines: the results of experimental data treatment by an iteration method using Eq. (X).

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