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The Kinetics and Mechanism of the Reversible Chain Reaction of Quinone Imine with Hydroquinone

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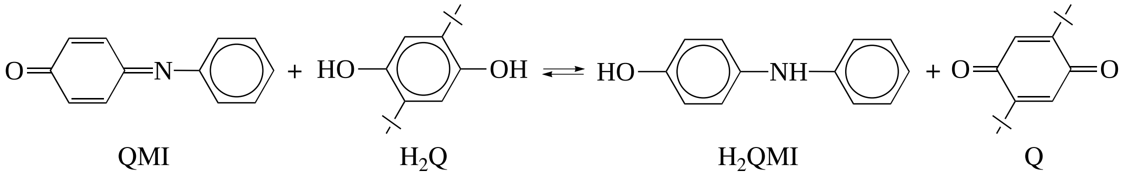
Abstract—The kinetics of the reaction of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-di-*tert*-butyl-1,4-hydroquinone in chlorobenzene was studied at 298.2 and 340 K. The previously proposed chain mechanism was confirmed and discussed. The rate constants and Arrhenius parameters of all elementary steps were determined or reliably estimated. Data on the possibility of radical formation by a termolecular reaction of quinone imine with two 4-hydroxydiphenylamine molecules were obtained, and the rate constant of this reaction was evaluated: $k = 0.22$ l^2 mol^{-2} s^{-1} at 298 K. The reversibility of all of the most important steps of this chain reaction (chain initiation, propagation, and termination) was demonstrated.

INTRODUCTION

The reactions of hydrogen atom transfer with the participation of quinones are of considerable interest for both chemistry and biology. Kinetic studies of these reactions started rather recently. In this case, in place of quinones, their nitrogen and seminitrogen analogs (quinone diimines and monoimines, respectively) are frequently used to considerably diminish experimental difficulties. Many substances were tested as the reducing agents of quinones (quinone imines) [1]. However, compounds with active hydrogen atoms, such as phenols (including hydroquinones) [2–4] and aromatic amines [5, 6], were used most frequently. The results obtained are contradictory, and the mechanisms of many reactions remain unclear. Thus, in some cases, the kinetics of reactions in quinone–hydroquinone systems can be adequately described in terms of the simple concept of a bimolecular reaction between components [4]. However, the above reaction kinetics is often inconsistent with this simplified concept [6].

In the last few years [7, 8], we found a chain mechanism in a reaction analogous to that in quinone–hydroquinone systems. This is the following reaction of *N*-phenyl-1,4-benzoquinone monoimine (QMI, a seminitrogen analog of quinone) with 2,5-di-*tert*-butyl-1,4-hydroquinone (H_2Q):



(I)

Reaction (I) results in the reduction of QMI by H_2Q, and the products are 4-hydroxydiphenylamine (H_2QMI) and 2,5-di-*tert*-butyl-1,4-quinone (Q).

This reaction was studied at only one temperature [7, 8]. Taking into account the importance of reactions in quinone–hydroquinone systems, we studied reaction (I) in more detail. In this study, the effect of temperature was examined, the set of experimental data was increased, and the range of reactant concentrations was extended in order to reveal new reactions that can occur in the system. Moreover, other techniques were used for data processing. Because of this, the numerical values of rate constants presented below are somewhat different from previously reported data [7, 8].

EXPERIMENTAL

The test quinone monoimine was synthesized by the oxidation of 4-hydroxydiphenylamine with PbO_2. The synthesis was performed in a glass column (5 × 0.8 cm) packed with PbO_2; an H_2QMI solution in diethyl ether was slowly passed through this column. The purification of QMI was performed by preparative liquid chromatography (LC) on SiO_2 (diethyl ether–hexane mixtures were used as an eluant) and by recrystallization from methanol. 2,5-Di-*tert*-butyl-1,4-hydroquinone, which was synthesized according to a published procedure [9], was kindly provided by I.K. Yakushchenko. This compound was additionally purified by LC on SiO_2 with the use of an ethyl acetate–benzene eluant.

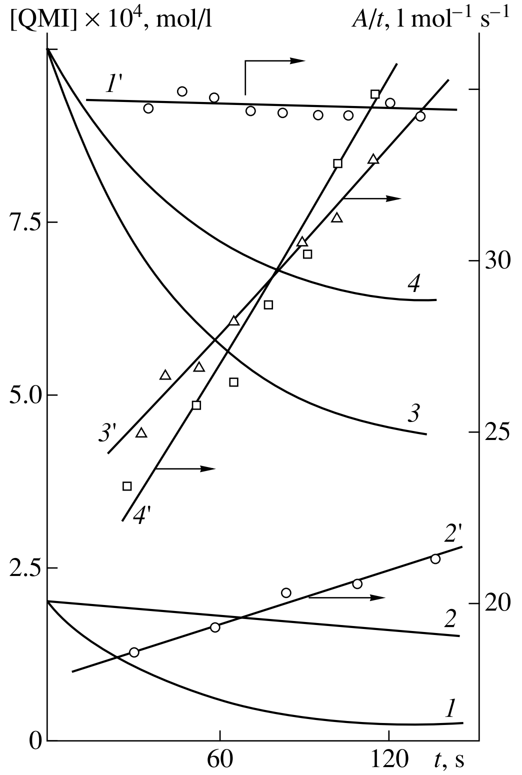


Fig. 1. (*1–4*) Kinetic curves of QMI consumption at 298.2 K and (*1'–4'*) their linearization in the A/t–t coordinates of Eq. (2). $[H_2Q] \times 10^4$: (*1*, *1'*) 6.0, (*2*, *2'*) 0.92, (*3*, *3'*) 6.0, and (*4*, *4'*) 3.6 mol/l.

Tetraphenylhydrazine (TPH) was synthesized according to Wieland by the oxidation of diphenylamine with $KMnO_4$ in acetone [10]. H_2QMI was purified by recrystallization from methanol and then from a mixture of heptane with toluene. The final purification of H_2QMI was performed by LC on SiO_2 with the use of diethyl ether–hexane mixtures as an eluant.

The solvent (chlorobenzene) was initially treated with H_2SO_4 and then with a saturated $KMnO_4$ solution in a ~25% aqueous NaOH solution. Thereafter, chlorobenzene was distilled in argon at a reduced pressure (T_b ~ 343 K). The residues of active impurities were removed with the use of tetraphenylhydrazine, which was added in a concentration of ~1 g/l [11]. Next, chlorobenzene was distilled at a reduced pressure and finally passed through a column (1 m × 3 cm) packed layer-by-layer with the following powders (bed length from the column inlet, cm): concentrated H_2SO_4 on SiO_2 (~15% H_2SO_4), 7; SiO_2, 1; $KMnO_4$ on Al_2O_3, 10; $CaCl_2$, 10; KOH, 10; and the remainder Brockmann I activated neutral Al_2O_3.

The kinetics of the reaction of QMI with H_2Q was studied by spectrophotometry usually at λ = const = 449 nm (22260 cm^{-1}), which corresponds to the absorption band maximum of QMI. The experiments were performed in a thermostatted bubbling-type quartz reactor cell (volume of 8.5 cm^3; optical path length of 2.0 cm) placed in a Specord UV–VIS spectrophotometer with continuously bubbling argon. The working temperatures were 298.2 ± 0.1 and 340.0 ± 0.5 K. The true reactant concentrations at 340 K were calculated with consideration for the thermal expansion of chlorobenzene (1×10^{-3} K^{-1}). The molar absorption coefficients of QMI at 298.2 and 340.0 K are equal to 2995 and 2920 l mol^{-1} cm^{-1}, respectively.

RESULTS AND DISCUSSION

Kinetics. The reaction of QMI with H_2Q at the chosen temperatures is quick, and almost irreversible (Fig. 1). The reaction has a complex mechanism. This follows from the two features given below. First, in the general case, the curves of consumption of the quinone imine QMI cannot be linearized in the coordinates of the second-order reaction rate equation

$$\frac{1}{[H_2Q]_0 - [QMI]_0}\ln\frac{[QMI]_0[H_2Q]}{[H_2Q]_0[QMI]} = k^{II}t, \qquad (1)$$

where k^{II} is the rate constant of a second-order reaction; $[QMI]_0$, $[H_2Q]_0$, [QMI], and $[H_2Q]$ are the initial and current reactant concentrations, respectively; and t is time.

For example, in experiments without additives of an initiator (and the reaction product H_2QMI), the coordinates of the following equation were found to be better suited for this purpose:

$$\frac{A}{t} = \text{const}_1 + \text{const}_2 t, \qquad (2)$$

where A is the right-hand side of Eq. (1), and const_1 and const_2 are empirical constants (Fig. 1). By this is meant that k^{II} in Eq. (1) increases with the degree of reaction (i.e., the test reaction is not a one-step reaction).

The other evidence for a complex mechanism consists in fractional orders n of the reaction with respect to reactants. It follows from Fig. 2 that n = 0.64–0.73 with respect to the quinone imine and n = 1.31–1.37 with respect to the hydroquinone at 298.2 K. The temperature affects these values only slightly, and the orders of the reaction with respect to QMI and H_2Q at 340 K are equal to 0.60–0.77 and 1.25–1.37, respectively.

Because of a complex mechanism of this reaction, its kinetics was studied and interpreted with the use of initial rates (w_{QMI}). To find w_{QMI}, kinetic curves were linearized in the coordinates of the empirical equation

$$\ln(a + \ln[QMI]) = b + ct, \qquad (3)$$

where *a*, *b*, and *c* are empirical constants. This equation was found applicable to all of the experiments. According to Eq. (3),

$$w_{\mathrm{QMI}} = -c[\mathrm{QMI}]_0(\ln[\mathrm{QMI}]_0 - a).$$

Table 1 summarizes some results obtained in this manner.

The published data [12–15] on the formation of free radicals in the reactions of quinones with hydroquinones in nonpolar solvents are of importance for interpreting the experimental data. On this basis, it was suggested that the observed complicated rate laws are a consequence of not only a simple radical mechanism but also of a chain reaction mechanism.

Initiator effect. To test the hypothesis of a chain mechanism, we directly introduced an initiator to the QMI + H_2Q system. We chose TPH as an initiator. Upon decomposition, this compound produces diphenylaminyl radicals $\mathrm{Ph_2N^{\bullet}}$ [16], which are highly active in the abstraction of H atoms from phenols, in particular, from the hydroquinone H_2Q ($k \sim 10^8$ l mol^{-1} s^{-1} [17]). Published data on $k^{\mathrm{TPH}}_{\mathrm{decomp}}$ are contradictory [18–20]. To improve the accuracy of experiments, we studied the kinetics of TPH decomposition in chlorobenzene with the use of *N*,*N*'-diphenyl-1,4-phenylenediamine as a scavenger of $\mathrm{Ph_2N^{\bullet}}$ radicals. The results are given in the table below.

T, K	$k^{\mathrm{TPH}}_{\mathrm{decomp}}$, s^{-1}*
298.2	2.06×10^{-7}
321.5	6.40×10^{-6}
343.7	1.03×10^{-4}
364.2	1.10×10^{-3}
383.2	7.71×10^{-3}

* The error is no higher than 1.5%.

In the Arrhenius form,

$$k^{\mathrm{TPH}}_{\mathrm{decomp}} = 10^{13.89 \pm 0.07} \exp(-117.5 \pm 0.6/RT)\ \mathrm{s}^{-1},$$

where E_a is expressed in kJ/mol. The probabilities *e* of radical escape into the bulk were determined at 364.2 and 383.2 K; they were found to be equal to $e = 0.95 \pm 0.015$ within the limits of experimental error. We used this value of *e* in the calculations of $k^{\mathrm{TPH}}_{\mathrm{i}}$ at 298.2 and 343.7 K; that is, we assumed that $k^{\mathrm{TPH}}_{\mathrm{i}} = 2ek^{\mathrm{TPH}}_{\mathrm{decomp}} = 1.90k^{\mathrm{TPH}}_{\mathrm{decomp}}$.

The reaction was strongly accelerated because of additional radical formation due to TPH decomposition (Fig. 3, Table 2). For example, at 298.2 K, an increase in the rate of initiation w_{i} due to TPH by ~10^{-9} mol l^{-1} s^{-1} resulted in an increase in w_{QMI} by ~10^{-6} mol l^{-1} s^{-1}. This fact indicates that the reaction of QMI with H_2Q proceeds via a chain mechanism, and it is characterized by very long chains of ~10^3 units. In the presence of TPH, the w_{QMH}–w_{i} relationships are adequately linearized in the w^2_{QMI}–w_{i} coordinates, and the intercepts on the axis of ordinates are positive (Fig. 3). Hence, it follows that the reaction of QMI with H_2Q in the presence of the initiator occurs in a mixed initiation mode and has quadratic chain termination. Evidently, in the absence of an initiator, chains are initiated because of processes occurring in the test system.

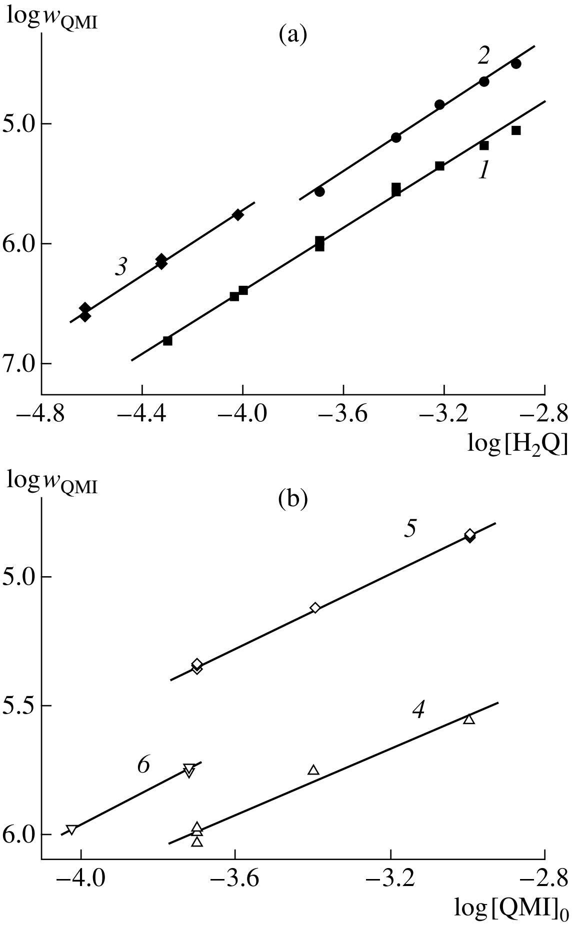


Fig. 2. Rates of quinone imine consumption as functions of (*1*–*3*) hydroquinone H_2Q and (*4*–*6*) quinone imine QMI concentrations in logarithmic coordinates at the initial concentrations (×10^4, mol/l): [QMI]$_0$, (*1*) 2.0, (*2*) 10.0, and (*3*) 1.9; [H_2Q]$_0$, (*4*) 2.0, (*5*) 6.0, and (*6*) 0.95. *T* = (*1*, *2*, *4*, *5*) 298.2 or (*3*, *6*) 340.0 K.

Reaction mechanism and discussion. The results were interpreted in terms of the mechanism that can be represented as the following kinetic scheme:

(**i**) $$\mathrm{TPH} \longrightarrow \mathrm{Ph_2N^{\bullet}} \longrightarrow \mathrm{HQ^{\bullet}},$$

(**1**) $$\mathrm{QMI} + \mathrm{H_2Q} \longrightarrow \mathrm{HQMI^{\bullet}} + \mathrm{HQ^{\bullet}},$$

(**2**) $$\mathrm{QMI} + \mathrm{HQ^{\bullet}} \longrightarrow \mathrm{HQMI^{\bullet}} + \mathrm{Q},$$

(**3**) $HQMI^{\bullet} + H_2Q \longrightarrow H_2QMI + HQ^{\bullet}$,

(**4**) $HQMI^{\bullet} + HQMI^{\bullet} \longrightarrow H_2QMI + QMI$,

(**5**) $HQMI^{\bullet} + HQ^{\bullet} \longrightarrow H_2QMI + Q(QMI + H_2Q)$,

(**6**) $HQ^{\bullet} + HQ^{\bullet} \longrightarrow H_2Q + Q$.

In this scheme, $HQMI^{\bullet}$ denotes radicals that are formed from the quinone imine QMI (or from H_2QMI) on the addition of an H atom (or hydrogen abstraction from H_2QMI). These can be either 4-hydroxydiphenylaminyl or 4-anilinophenoxy radicals; for simplicity, they are considered as indistinguishable.

Let us consider the proposed mechanism and discuss its most important steps. According to the above scheme, chain initiation in the absence of an initiator takes place according to reaction (**1**) by the direct reaction of QMI with H_2Q, and chain termination occurs at steps (**4**)–(**6**) by the homo- and cross-disproportionation of $HQMI^{\bullet}$ and $HQ^{\bullet}$ radicals. Initiation step (**1**) and chain-termination step (**5**) are forward and reverse elementary reactions, respectively. Undoubtedly, chain-termination steps (**4**) and (**6**) are reversible, and both of the reverse reactions are initiation reactions. The reversibility of steps (**4**)–(**6**) can be ignored at low degrees of conversion (i.e., when the initial rates w_{QMI} are used). This is not true at high degrees of conversion, as indicated by a continuous increase in the apparent second-order rate constant k^{II} in the course of reaction (see Fig. 1). In terms of the above scheme, the reaction of QMI with H_2Q is thus considered as a chain process with the reversible steps of chain termination. It is also true that the reaction of QMI with H_2Q can be considered as a degenerate branching chain reaction with chain branching at stable final products.

Proposed steps (**2**) and (**3**) of chain propagation are worthy of special consideration. It is clear that the rate constants of these reactions are high because only in this case these reactions can compete with almost diffusion-controlled steps (**4**)–(**6**). Undoubtedly, the 4-hydroxydiphenylaminyl radicals $HQMI^{\bullet}$ (i.e., $Ph–N^{\bullet}–C_6H_4OH$) are involved in reaction (**3**) of the interaction of QMI with H_2Q. This conclusion may be drawn from

Table 1. Effects of reactant concentrations and temperature on the initial reaction rate w_{QMI} and the chain length ν

$[QMI]_0 \times 10^4$, mol/l	$[H_2Q]_0 \times 10^4$, mol/l	$w_{QMI} \times 10^6$, mol l^{-1} s^{-1}	$\nu^{*}_{expt} \times 10^{-3}$	$\nu^{**}_{calcd} \times 10^{-3}$
298.2 K				
1.00	2.00	0.68	5.28	5.20
2.00	0.50	0.15	2.33	2.43
"	1.00	0.41	3.18	3.27
"	2.00	1.07	4.15	4.23
"	4.00	2.70	5.24	5.20
"	6.00	4.30	5.56	5.72
4.00***	2.00	1.76	3.42	3.27
"	6.00	7.49	4.85	4.81
"	12.00	17.83	5.77	5.72
10.00****	2.00	2.76	2.14	2.20
"	6.00	14.30	3.70	3.51
"	12.00	31.69	4.10	4.49
340.0 K				
0.95	0.2375	0.178	0.46	0.46
"	0.950	1.05	0.68	0.69
1.90	0.2075	0.267	0.34	0.34
"	0.475	0.701	0.45	0.46
"	0.950	1.786	0.57	0.57

* $\nu_{expt} = \dfrac{w_{QMI}}{2k_1[QMI]_0[H_2Q]_0}$.

** ν_{calcd} calculated by Eq. (10).

*** Determined at $\lambda = 403.4$ nm; $\varepsilon = 1631$ l mol^{-1} cm^{-1}.

**** Determined at $\lambda = 383.2$ nm; $\varepsilon = 563$ l mol^{-1} cm^{-1}.

an analysis of published data [21, 22], which demonstrates that aminyl radicals are much more reactive than phenoxy radicals (i.e., $\mathrm{Ph{-}NH{-}C_6H_4{-}O^{\bullet}}$) in the reactions of hydrogen abstraction from phenols. In this case, the rate constant of the assumed reaction can be evaluated by the relationship [17]

$$\log k_3\ (294\ \mathrm{K,\ decane}) = (6.38 - 0.69\sigma^{+}) + (0.127 + 0.026\sigma^{+})q,$$

where σ^+ is the Brown constant for a *para*-substituent in the diphenylaminyl radical (σ^+(OH) = –0.853 [23]) and q is the heat effect of the reaction (kJ/mol). The dissociation energy of the N–H bond in H_2QMI, which is required for estimating q, can be found using the relation [24]

$$D_{\mathrm{NH}},\ \mathrm{kJ/mol} = 363.6 + 11.93\sigma^{+} = 363.6 + 11.93(-0.85) = 353.4.$$

The value of D_{OH} in H_2Q is equal to 345.1 kJ/mol [17]; then, $q = D_{\mathrm{NH}} - D_{\mathrm{OH}} = 8.3$ kJ/mol and $\log k_3$ (294 K, decane) = 7.84. Thus, in decane, $k_3 \approx 6.9 \times 10^7\ \mathrm{l\ mol^{-1}\ s^{-1}}$ on a per-group basis and $k_3 \approx 1.4 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$ on an H_2Q molecule basis. It should be expected that the value of k_3 in chlorobenzene will be somewhat lower than that in decane because phenols form H-complexes with the aromatic solvent [25]. The corresponding corrections can be evaluated using hydrogen bond parameters [26], and the expected value of k_3 in chlorobenzene was found to be $\sim(2.5\text{–}4) \times 10^7\ \mathrm{l\ mol^{-1}\ s^{-1}}$. Such a high value of k_3 provides support for the hypothesis that reaction (**3**) can be considered as a chain-propagation step. Note that the experimentally found rate constant k_3 differs from this estimate by a factor of only two (see below).

We proposed reaction (**2**) as another step of chain propagation in the scheme [7]. In due time, we introduced this reaction, that is, suggested that the value of k_2 is high, based on only indirect evidence given in [27, 28]. In these publications, it was found that even a weak oxidizing agent such as molecular oxygen can abstract H atoms from semiquinone radicals analogous to $\mathrm{HQMI^{\bullet}}$ and $\mathrm{HQ^{\bullet}}$: the rate constants of these reactions are equal to $\sim10^2\ \mathrm{l\ mol^{-1}\ s^{-1}}$ at ~340 K, although the reactions are strongly endothermic. The quinone imine QMI is a much stronger oxidizing agent as compared with O_2; reaction (**2**) of QMI with $\mathrm{HQ^{\bullet}}$ is almost thermoneutral. This fact suggests that the value of k_2 may be high.

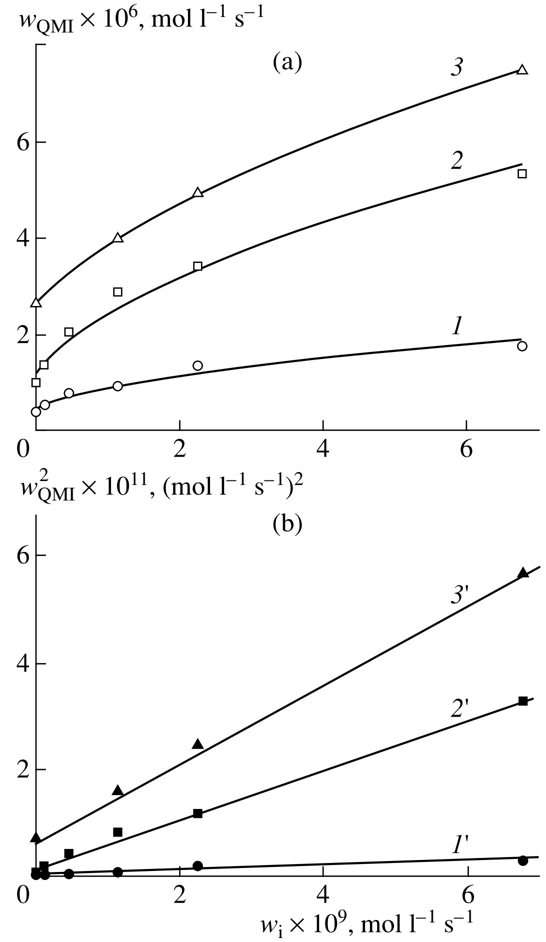


Fig. 3. (*1–3*) Rates of the reaction of QMI with H_2Q as functions of the rate of initiation in the presence of tetraphenylhydrazine and (*1'–3'*) linearization of curves *1–3* in the w^2_{QMI}–w_{i} coordinates. $[\mathrm{QMI}]_0$ = const = 2×10^{-4} mol/l. $[\mathrm{H_2Q}]_0 \times 10^4$, mol/l: (*1*) 1.0, (*2*) 2.0, and (*3*) 4.0. T = 298.2 K.

Let us derive quantitative relationships from the above scheme. Note that reaction (**6**) can be neglected, as found by data treatment within the framework of the full scheme. Taking into account this note, based on the equation for long chains

$$w_{\mathrm{QMI}} = k_2[\mathrm{QMI}][\mathrm{HQ^{\bullet}}] = k_3[\mathrm{HQMI^{\bullet}}][\mathrm{H_2Q}], \quad (4)$$

we obtain the following expressions for radical concentrations:

$$[\mathrm{HQ^{\bullet}}] = \frac{w_{\mathrm{QMI}}}{k_2[\mathrm{QMI}]}, \quad [\mathrm{HQMI^{\bullet}}] = \frac{w_{\mathrm{QMI}}}{k_3[\mathrm{H_2Q}]}. \quad (5)$$

Substituting (5) into the steady-state equation

$$k_1[\mathrm{QMI}][\mathrm{H_2Q}] + 0.5w_{\mathrm{i}} = k_4[\mathrm{HQMI^{\bullet}}]^2 + k_5[\mathrm{HQMI^{\bullet}}][\mathrm{H_2Q^{\bullet}}], \quad (6)$$

we obtain the rate equation

$$w_{QMI}^2 = \frac{k_2k_3^2[QMI][H_2Q]^2(k_1[QMI][H_2Q] + 0.5w_i)}{k_2k_4[QMI] + k_3k_5[H_2Q]}. \quad (7)$$

In the absence of an initiator, that is, at $w_i = 0$,

$$\left(\frac{[QMI][H_2Q]^2}{w_{QMI}}\right) = \frac{k_5}{k_1k_2k_3} + \frac{k_4}{k_1k_3^2}\frac{[QMI]}{[H_2Q]}. \quad (8)$$

Figure 4 demonstrates experimental data obtained without initiator; these data are plotted in the coordinates of Eq. (8). It can be seen that all points lie along a straight line, although w_{QMI} is dramatically changed: by a factor of 200 or by more than one order of magnitude in experiments at 298.2 or 340.0 K, respectively. The statistical treatment gives the following:

Parameter	298.2 K	340.0 K
$\frac{k_5}{k_1k_2k_3}$, (mol s $l^{-1})^2$	$(4.5 \pm 0.5) \times 10^{-4}$	$(4.2 \pm 1.2) \times 10^{-5}$
$\frac{k_4}{k_1k_3^2}$, (mol s $l^{-1})^2$	$(9.4 \pm 0.3) \times 10^{-4}$	$(3.1 \pm 0.2) \times 10^{-5}$

For simplicity, we introduced the parameter $\alpha = k_3k_5/(k_2k_4)$. Its numerical values were found from the above data: $\alpha = 0.48 \pm 0.07$ and 1.37 ± 0.48 at 298.2 and 340.0 K, respectively. Using this parameter and taking into account that $w_i = 2ek_{decomp}^{TPH}$ [TPH], the following

Table 2. Dependence of the initial rate and the chain length of the reaction of QMI with H_2Q on the rate of initiation in the presence of TPH

$[QMI]_0 \times 10^4$	$[H_2Q]_0 \times 10^4$	$w_i \times 10^9$	$w_{QMI} \times 10^6$	$\nu_{expt}^{*} \times 10^{-3}$	$\nu_{calcd}^{**} \times 10^{-3}$
mol/l		mol l^{-1} s^{-1}			
298.2 K					
2.00	2.00	0.112	1.37	3.71	3.55
		0.450	2.05	2.90	2.55
		2.25	3.44	1.37	1.36
	6.00	0.112	4.81	5.44	5.34
		1.12	7.78	4.11	3.65
		2.25	8.65	2.86	2.89
10.00	2.00	0.112	3.29	2.35	2.11
		1.12	3.70	1.54	1.61
		6.75	6.54	0.81	0.88
	12.00	0.450	32.1	3.93	4.37
		2.25	36.1	3.62	3.95
		6.75	41.1	2.84	3.28
340.0 K					
1.90	0.2375	0.777	0.39	0.251	0.244
		1.56	0.46	0.197	0.199
		3.11	0.60	0.154	0.154
	0.475	0.777	0.88	0.378	0.372
		1.56	1.02	0.328	0.321
		3.11	1.15	0.247	0.263

* $\nu_{expt} = \frac{w_{QMI}}{2k_1[QMI][H_2Q] + w_i}$.

** ν_{calcd} calculated by Eq. (10a).

expression is derived from Eq. (7) for processing data obtained in the presence of the initiator:

$$\frac{[\mathrm{QMI}]+\alpha[\mathrm{H_2Q}]}{[\mathrm{QMI}]^2[\mathrm{H_2Q}]^3}w_{\mathrm{QMI}}^2 = \frac{k_1k_3^2}{k_4} + \frac{ek_{\mathrm{decomp}}^{\mathrm{TPH}}k_3^2}{k_4}\frac{[\mathrm{TPH}]}{[\mathrm{QMI}][\mathrm{H_2Q}]}$$

or

$$Z = \frac{k_1k_3^2}{k_4} + \frac{ek_{\mathrm{decomp}}^{\mathrm{TPH}}k_3^2}{k_4}X. \qquad (9)$$

As Fig. 5 demonstrates, Eq. (9) is consistent with experimental results. The parameters of straight lines in Fig. 5 have the following values:

Parameter	298.2 K	340.0 K
$\frac{k_1k_3^2}{k_4}$, $(\mathrm{l\ mol^{-1}\ s^{-1}})^2$	$(1.09 \pm 0.05) \times 10^3$	$(3.3 \pm 0.1) \times 10^{-4}$
$\frac{ek_{\mathrm{decomp}}^{\mathrm{TPH}}k_3^2}{k_4}$, $\mathrm{l\ mol^{-1}\ s^{-2}}$	$(6.5 \pm 0.15) \times 10^{-2}$	25.0 ± 0.6

With consideration for the above data on $k_{\mathrm{decomp}}^{\mathrm{TPH}}$, we obtain

Parameter	298.2 K	340.0 K
$\frac{k_3^2}{k_4}$, $\mathrm{l\ mol^{-1}\ s^{-1}}$	$(3.4 \pm 0.4) \times 10^5$	$(3.8 \pm 0.3) \times 10^5$
k_1, $\mathrm{l\ mol^{-1}\ s^{-1}}$	$(3.2 \pm 0.2) \times 10^{-3}$	$(8.6 \pm 0.5) \times 10^{-2}$

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

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

The dissociation energy of the O–H (or N–H) bond in the H–QMI$^\bullet$ radical can be estimated from the obtained value of E_1 on the assumption that the activation energy of reaction (**1**) in the scheme is insignificantly different from the enthalpy of reaction, as is the case in other similar reactions [29]. We obtain $D_{\mathrm{H-QMI^\bullet}} \approx D_{\mathrm{OH}}(\mathrm{H_2Q}) - E_1 = 345.1 - 66.2 \approx 279$ kJ/mol, which is consistent with a previous estimate of 284.5 kJ/mol [5]. Note that the O–H bond strength in the simplest semiquinone radical 4-hydroxyphenoxy was much lower and equal to only 226.1 kJ/mol as calculated from the heats of combustion of quinone and hydroquinone [30]. The reason for such a dramatic difference between this estimate and the value of $D_{\mathrm{H-QMI}}$ obtained by us remains unclear.

Assuming that $k_4 = k_5 = 8 \times 10^8\ \mathrm{l\ mol^{-1}\ s^{-1}}$ (the average value of insignificantly different k values for the reactions of a number of other semiquinone radicals

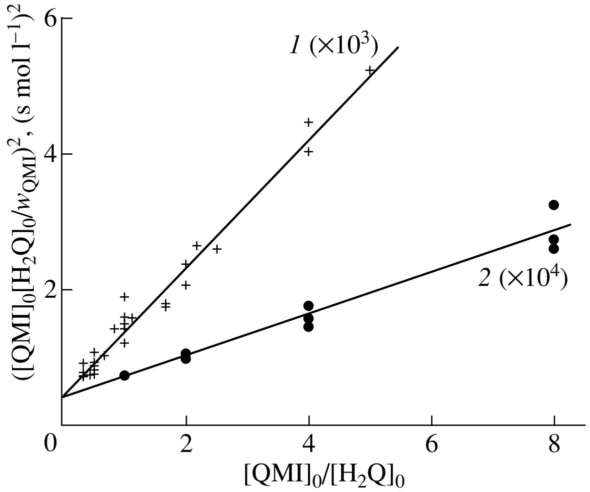


Fig. 4. Treatment of the results of experiments performed in the absence of an initiator in the coordinates of Eq. (8). T = (*1*) 298.2 or (*2*) 340.0 K.

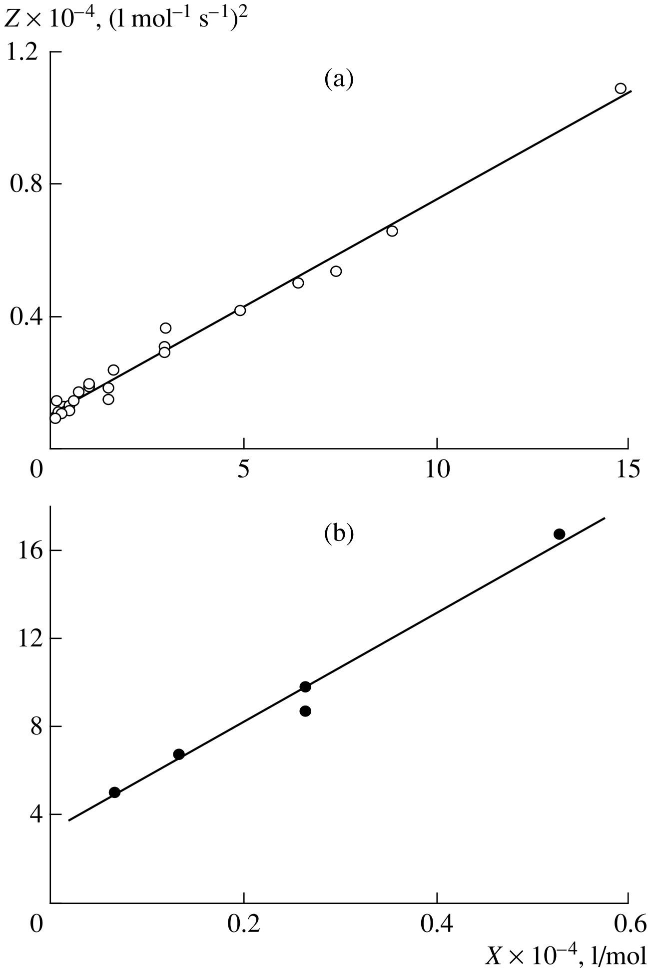


Fig. 5. Treatment of the results of experiments performed in the presence of an initiator with the use of Eq. (9). T = (*1*) 298.2 or (*2*) 340.0 K.

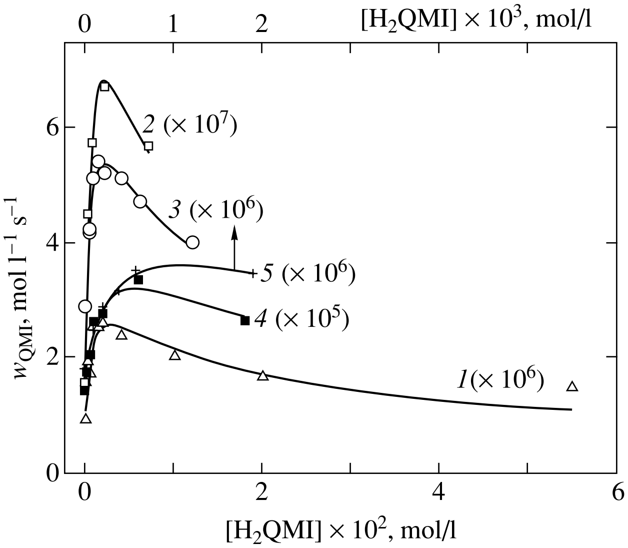


Fig. 6. Initial reaction rate as a function of the concentration of the final product H_2QMI at $[\text{QMI}]_0 \times 10^4$ and $[H_2Q] \times 10^4$ (mol/l), respectively: (*1*) 2.0 and 2.0, (*2*) 2.0 and 0.5, (*3*) 2.0 and 4.0, (*4*) 10.0 and 6.0, or (*5*) 1.9 and 0.95. T = (*1–4*) 298.2 or (*5*) 340.0 K. Points: experimental data. Lines: calculations by Eq. (11) at the values of k_{-3} and k_{-4} specified in Table 4.

[31, 32]), the absolute values of k_3 and $k_2 = k_3/\alpha$ can be found. In this case, the rate constants can be determined or reliably estimated for all steps in the scheme under consideration (Table 3). The value of k_3 in Table 3 is consistent with the above estimate. As expected, the value of k_2 is very high (~10^7 l mol^{-1} s^{-1}). Both chain-propagating steps (**2**) and (**3**) are characterized by near-zero or even small negative activation energies. In the case of step (**3**), this fact is consistent with published data obtained for the reactions of aminyl radicals with phenols [25].

The chain mechanism can explain the fractional orders of reaction with respect to components. It follows from Eq. (7) that in the absence of an initiator the expected values of n_{QMI} and n_{H_2Q} lie within the ranges $0.5 < n_{\text{QMI}} < 1$ and $1 < n_{H_2Q} < 1.5$, respectively. This is in complete agreement with experimental data.

The average number of QMI molecules converted into H_2QMI per one radical generated in the system can be considered as the measure of chain length ν. Then, we obtain the following expressions for ν in uninitiated and initiated reactions:

$$\nu = \frac{w_{\text{QMI}}}{w_{\text{i}}} = \frac{k_3}{2k_1^{1/2}}\left(\frac{k_2[H_2Q]}{k_2k_4[\text{QMI}] + k_3k_5[H_2Q]}\right)^{1/2}, \quad (10)$$

$$\nu = \frac{w_{\text{QMI}}}{w_{\text{i}}} = \frac{k_3[H_2Q]}{2(k_1[\text{QMI}][H_2Q] + 0.5w_{\text{i}})^{1/2}} \times \left(\frac{k_2[\text{QMI}]}{k_2k_4[\text{QMI}] + k_3k_5[H_2Q]}\right)^{1/2}. \quad (10a)$$

Tables 1 and 2 summarize the values of ν. In the absence of an initiator, the chain length is equal to several thousands of units at 298.2 K or to several hundreds at 340 K. Because reactant concentrations in the experiments performed at 298.2 and 340 K were insignificantly different, an increase in w_{i} should be considered as the main reason for a decrease in ν with temperature because of a considerable increase in k_1.

The dual effect of the final product H_2QMI. Additional data on the reaction of QMI with H_2Q were obtained in a study of the dependence of the reaction rate on the concentration of the final product H_2QMI. Figure 6 indicates that small additives (~10^{-4} mol/l) of H_2QMI accelerate the reaction; however, at higher concentrations, its inhibiting effect becomes stronger. Because of such a dual effect, the plots of w_{QMI} as a function of H_2QMI concentration exhibit the shapes of curves with a maximum.

Because the reaction of QMI with H_2Q proceeds via a chain mechanism, there is no doubt that an increase in the rate of initiation in the presence of H_2QMI is responsible for the accelerating effect of this com-

Table 3. Rate constants of the elementary steps of a chain reaction between the quinone imine QMI and the hydroquinone H_2Q in chlorobenzene

Step	Reaction	k, l mol^{-1} s^{-1}	
		298.2 K	340.0 K
(**1**)	$\text{QMI} + H_2Q \longrightarrow \text{HQMI}^\bullet + \text{HQ}^\bullet$	3.22×10^{-3}	8.61×10^{-2}
(**2**)	$\text{QMI} + \text{HQ}^\bullet \longrightarrow \text{HQMI}^\bullet + \text{Q}$	3.47×10^{7}	1.28×10^{7}
(**3**)	$\text{HQMI}^\bullet + H_2Q \longrightarrow H_2\text{QMI} + \text{HQ}^\bullet$	1.65×10^{7}	1.75×10^{7}
(**4**)	$\text{HQMI}^\bullet + \text{HQMI}^\bullet \longrightarrow H_2\text{QMI} + \text{QMI}$	8×10^{8}*	8×10^{8}*
(**5**)	$\text{HQMI}^\bullet + \text{HQ}^\bullet \longrightarrow \text{QMI} + H_2O\ (H_2\text{QMI} + \text{Q})$	8×10^{8}*	8×10^{8}*

* By hypothesis.

pound. As mentioned above, steps (**1**) and (**5**) are mutually inverse and play opposite roles in the chain process: reaction (**1**) is an initiation step, whereas reaction (**5**) is a chain-termination step. There is no doubt that the reversibility of an additional step of chain termination in the presence of H_2QMI manifests itself from the very beginning and the following chain-initiation reaction is responsible for the accelerating effect of H_2QMI on the reaction of QMI with H_2Q:

$$(\mathbf{-4})\qquad H_2QMI + QMI \longrightarrow HQMI^{\bullet} + HQMI^{\bullet}.$$

This assumption is also consistent with an experimentally observed increase in the apparent second-order reaction rate constant k^{II} in the course of reaction, that is, as products (in particular, H_2QMI, see Fig. 1) are accumulated in the system.

Undoubtedly, an opposite inhibiting effect of H_2QMI results from a decrease in the chain length. We assumed that ν and the rate of the overall reaction decreased in the presence of H_2QMI because of the reversibility of reaction (**3**) rather than as a consequence of new termination reactions. The reaction

$$(\mathbf{-3})\qquad HQ^{\bullet} + H_2QMI \longrightarrow H_2Q + HQMI^{\bullet}$$

can dramatically inhibit the overall chain process because the rate constant of this reaction (on the assumption that $HQ^{\bullet}$ attacks only the N–H bond in H_2QMI) was estimated to be very high:

$$k_{-3}(298.2\text{ K}) = K_{-3}k_3 \approx k_3\exp(-\Delta H_{-3}/RT)$$
$$\approx 2.4 \times 10^6\text{ l mol}^{-1}\text{ s}^{-1},$$

where K_{-3} is the equilibrium constant of reaction (**–3**).

Supplementing the scheme with steps (**–3**) and (**–4**), we obtain the simplest mechanism of the reaction of QMI with H_2Q in the presence of H_2QMI. In this case, the reaction rate is expressed as follows:

$$w^2_{QMI} = \frac{AB}{C+D}, \tag{11}$$

where

$$A = k_2^2k_3^2[QMI]^3[H_2Q]^2,$$

$$B = k_1[H_2Q] + k_{-4}[H_2QMI],$$

$$C = k_4(k_2[QMI] + k_{-3}[H_2QMI])^2,$$

$$D = k_3k_5[H_2Q](k_2[QMI] + k_{-3}[H_2QMI]).$$

Equation (11) contains only two unknown constants k_{-3} and k_{-4}, which can be found from experimental data with the use of iteration methods. Table 4 summarizes the results obtained. As can be seen, the value $k_{-3} = 3.5 \times 10^6$ l mol^{-1} s^{-1} at 298.2 K given in Table 4 is insignificantly different from the above estimate. The activation energy of the reaction is close to zero: $E_{-3} = -5.4 \times 4.1$ kJ/mol. Thus, it seems reasonable that reaction (**–3**) is not a one-step reaction, and it is preceded by the step of formation of an intermediate complex due to hydrogen bonds. As expected, the kinetic parameters of reaction (**–4**) are close to the parameters previously found for similar reaction (**1**), namely:

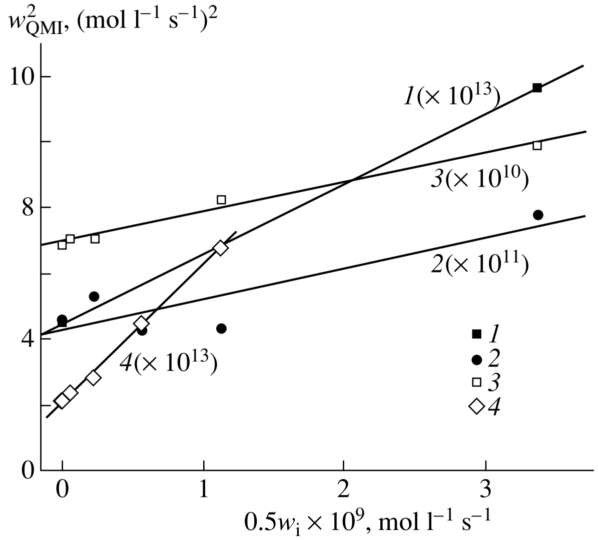


Fig. 7. Treatment of experimental data obtained in a study of the reaction of QMI with H_2Q in the simultaneous presence of H_2QMI and the TPH initiator in the coordinates of Eq. (12). [QMI] × 10^4, $[H_2Q]_0$ × 10^4, and $[H_2QMI]_0$ × 10^3 (mol/l), respectively: (*1*) 2.0, 0.5, and 2.0; (*2*) 2.0, 6.0, and 2.0; (*3*) 10.0, 6.0, and 1.0; (*4*) 2.0, 0.5, and 0.2. T = 298.2 K.

$$k_{-4} = 10^{8.20 \pm 0.56}\exp((-59.4 \pm 3.4)/RT)\text{ l mol}^{-1}\text{ s}^{-1},$$

where the activation energy is expressed in kJ/mol.

Both of the constants k_{-3} and k_{-4} at 298.2 K were also independently determined from experiments performed in the simultaneous presence of H_2QMI and the TPH initiator (double mixed initiation mode). In this case, the (squared) rate of the reaction is expressed in the following form:

$$w^2_{QMI} = \frac{AB}{C+D} + \frac{A}{[QMI]_0(C+D)}\frac{w_i}{2} \tag{12}$$

or,

$$w^2_{QMI} = x + y\frac{w_i}{2},$$

where parameters *A*–*D* are the same as in Eq. (11). Indeed, as can be seen in Fig. 7, straight lines appear in the w^2_{QMI}–$w_i/2$ coordinates of Eq. (12). The values of k_{-3} can be found from the slopes y of these straight lines, whereas the absolute values of k_{-4} can also be determined from the intercepts x on the axis of ordinates with the use of known k_{-3} (found from the value of y). Table 5 summarizes the results thus obtained. A comparison of these results with the corresponding data

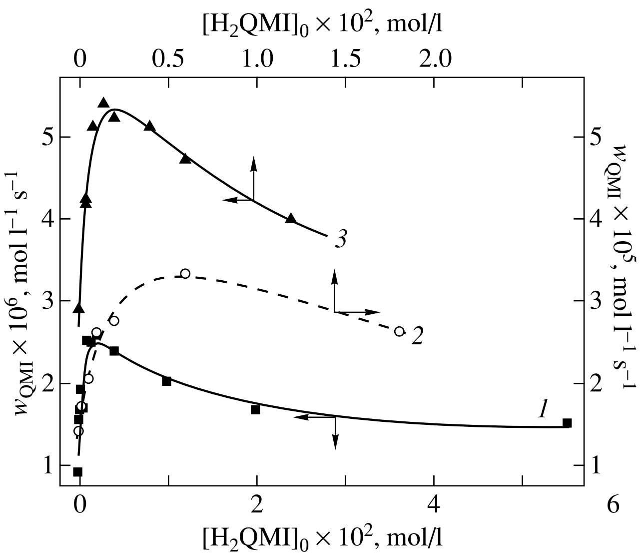


Fig. 8. Treatment of experimental data on the effect of H_2QMI on the initial reaction rate w_{QMI} with the use of Eq. (13). $[QMI]_0$ and $[H_2Q]_0 \times 10^4$ (mol/l), respectively: (*1*) 2.0 and 2.0, (*2*) 10.0 and 6.0, (*3*) 2.0 and 4.0. T = 298.2 K. Points: experimental data. Lines: calculations at the values of k_{-3}, k_{-4}, and k_7 specified in Table 4.

in Table 4 demonstrates that both of the methods gave similar values. It is likely that a higher accuracy in k_{-3} and k_{-4} cannot be attained because the absolute values of the rate constants of reactions in the scheme supplemented with reactions (**–3**) and (**–4**) are dramatically different (by almost 10 orders of magnitude).

Termolecular initiation reaction. Figure 6 demonstrates that curves calculated by Eq. (11) increasingly deviate from experimental points as the concentration of H_2QMI increases. We assumed that the reason for this is the following termolecular reaction of radical formation, which was not taken into account in the mechanism:

$$(\mathbf{7}) \qquad \mathrm{HQMI} + \mathrm{QMI} + \mathrm{HQMIH} \longrightarrow \mathrm{HQMI}^{\bullet} + \mathrm{HQMIH} + {}^{\bullet}\mathrm{QMIH}.$$

Termolecular reactions of this kind are not rare; in particular, a number of such reactions are presently known to occur in chain oxidation processes [33]. If the mechanism is supplemented with step (**7**), Eq. (11) for the reaction rate takes the form

$$w_{QMI}^2 = \frac{A(B + k_7[H_2QMI]^2)}{C + D}. \qquad (13)$$

The experimental data were treated once again with the use of Eq. (13). The sets of rate constants k_{-3}, k_{-4}, and k_7 were obtained for each series of experiments, and these data are given in the last columns of Table 4. Note that in the search of these constants no restrictions were imposed on their values. In this context, it seems even surprising that the values of k_{-3}, k_{-4}, and k_7 rate constants in separate series are consistent both with each other and with data previously found using

Table 4. Rate constants k_{-3}, k_{-4}, and k_7 calculated by numerical methods with the use of experimental relationships between w_{QMI} and the concentration of the H_2QMI additive in experimental runs performed at $[QMI]_0$, $[H_2Q]_0$ = const

$[QMI]_0$	$[H_2Q]_0$	$[H_2QMI]$, mol/l	$k_{-3} \times 10^{-6}$	$k_{-4} \times 10^3$	$k^*_{-3} \times 10^{-6}$	$k^*_{-4} \times 10^3$	k_7, l^2 mol^{-2} s^{-1}
$\times 10^4$, mol/l			l mol^{-1} s^{-1}				
298.2 K							
2	2	$0–5.5 \times 10^{-2}$	2.78	4.60	3.95	5.73	0.169
2	0.5	$0–7.0 \times 10^{-3}$	3.84	6.36	4.95	7.10	0.417
2	4	$0–1.2 \times 10^{-2}$	3.95	8.18	4.30	8.57	0.100
10	6	$0–1.8 \times 10^{-2}$	3.52	6.38	–	–	–
Average			3.52 ± 0.26	6.38 ± 0.73	4.40 ± 0.29	7.13 ± 0.82	0.229 ± 0.096
340.0 K							
1.9	0.95	$0–1.9 \times 10^{-3}$	2.54	103	2.72	105	3.58
1.9	0.2375	$0–9.5 \times 10^{-4}$	3.90	136	–	–	–
1.9	0.475	$0–1.9 \times 10^{-3}$	2.28	92	–	–	–
0.95	0.2375	$0–3.8 \times 10^{-4}$	3.42	154	–	–	–
Average			3.03 ± 0.38	121.3 ± 14.4	–	–	–

* The values were obtained with consideration for step (**7**).

Table 5. Values of parameters X and Y in Eq. (12) determined from Fig. 7, and rate constants k_{-3} and k_{-4} calculated using the above parameters

Straight line in Fig. 7	$[QMI]_0 \times 10^4$	$[H_2Q]_0 \times 10^4$	$[H_2QMI]_0 \times 10^3$	$x \times 10^{12}$, $(mol\ l^{-1}\ s^{-1})^2$	$y \times 10^4$, $mol\ l^{-1}\ s^{-1}$	$k_{-3} \times 10^{-6}$	$k_{-4} \times 10^3$
	mol/l					$l\ mol^{-1}\ s^{-1}$	
1	2	0.5	2	0.45 ± 0.01	2.12 ± 0.05	3.28	5.19
2	2	6	2	42.9 ± 0.5	93.4 ± 30.6	6.86	10.5
3	10	6	1	699 ± 11	890 ± 67	1.36	5.92
4	2	0.5	0.2	0.21 ± 0.01	4.19 ± 0.12	12.7	11.5
Average						6.1 ± 2.5	8.3 ± 1.6

Eq. (11). A comparison between Figs. 6 and 8 indicates that Eq. (13) better describes the experimental w_{QMI}–$[H_2QMI]_0$ relations than Eq. (11) does, especially, at high concentrations of H_2QMI. The temperature dependence of rate constants k_{-4} and k_7 can be expressed as follows (activation energies, kJ/mol):

$$k_{-4} = 10^{7.4 \pm 0.8}\exp((-54.5 \pm 4.7)/RT)\ l\ mol^{-1}\ s^{-1}$$

$$k_7 = 10^{9.6 \pm 2.9}\exp((-59.0 \pm 16.8)/RT)\ l\ mol^{-1}\ s^{-1}.$$

Termolecular reaction (**7**) is a reaction with a concerted bond rupture; in the transition state, two H–QMIH bonds are simultaneously ruptured, and N–H and O–H bonds are formed. It is clear that the heat effect of reaction (**7**) is insignificantly different from the heat effect of reaction (**–4**). In this case, the activation energy of the reaction is $E_7 \approx E_{-4} + \Delta E$, where $\Delta E = RT\ln(\pi E_{-4}/3RT) \sim 8$ kJ/mol at 300 K is the additional energy consumption due to the concerted bond rupture [34]. The preexponential factor of reaction (**7**) is lower than that of bimolecular reaction (**–4**) [34]: $A_7 = A_{-4}P(E) = A_{-4}(2RT/\pi E)^{1/2} \sim 0.17A_{-4}$ at 300 K, and E = 55 kJ/mol, where $P(E)$ is the probability of concerted energy concentrating on two bonds being broken. The estimates obtained are consistent with experimental results, the especially due to the low accuracy.

CONCLUSION

Thus, this study indicates a chain mechanism of the reaction of the quinone imine with the hydroquinone. The results indicate that a new termolecular reaction can take place with the generation of $HQMI^{\bullet}$ semiquinone radicals by the interaction of the quinone imine QMI with two 4-hydroxydiphenylamine molecules (H_2QMI). The rate constants of all of the elementary steps were obtained or reliably estimated, and their temperature dependence parameters were found. Only bimolecular and termolecular initiation reactions are characterized by high activation energies of ~55–60 kJ/mol, whereas the activation energies of the steps of propagation and chain termination are close to zero. The proposed mechanism is in complete agreement with experimental data. The reversibility of all key steps (chain initiation, propagation, and termination) of the test reaction was experimentally proven. Only the reversibility of step (**2**) remained unproved, although the results of this study and available published data undoubtedly suggest the reversibility of this step and the occurrence of reverse reaction (**–2**) under real experimental conditions, particularly, at deep conversions and/or in the presence of the quinone Q added. Because all of the elementary steps are reversible, the reaction of QMI with H_2O can be considered as an overall reversible chain reaction. With such a mechanism, the state of (thermodynamic) reaction equilibrium can be attained via a chain path starting from either the initial reactants or the reaction products. In this equilibrium, none of the steps of both forward and reverse chain reactions is terminated.

The extremely high activity of the quinone imine in hydrogen abstraction from the semiquinone radical $HQ^{\bullet}$ is primarily responsible for the occurrence of a chain mechanism. We measured the rate constant of this almost thermoneutral reaction for the first time; this rate constant is very high: $k \sim 10^7\ l\ mol^{-1}\ s^{-1}$. Undoubtedly, quinone imines (and quinones as their oxygen analogs) also very rapidly react with other reducing radicals, particularly, if such reactions are exothermic.

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