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CHEMICAL KINETICS AND CATALYSIS

The Kinetics of the Reversible Chain Reaction between 2,5-Dichloroquinone and 4-Hydroxydiphenylamine

A. V. Antonov and V. T. Varlamov

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, 142432 Russia e-mail: varlamov@icp.ac.ru

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Abstract—The paper presents the results obtained in a study of the kinetics of the reversible chain reaction between 2,5-dichloroquinone and 4-hydroxydiphenylamine ($K_{eq} = 3.2$). We studied the dependence of the reaction rate on the concentrations of the initiator, initial reagents, and all products. The equations obtained earlier for the rate of reversible chain reactions and the method of equal concentrations suggested in this work were used to estimate the rate constants of most of the reaction mechanism elementary steps from the experimental data. The results obtained were shown to closely agree with and augment the data obtained earlier for the kinetics of the chain reaction between N-phenyl-1,4-benzoquinonemonoimine and 2,5-dichlorohydroquinone. On the whole, all the elementary steps of these two (forward and back) reversible chain reactions were characterized by rate constant values.

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INTRODUCTION

In [1], we experimentally substantiated the suggestion [2, 3] that reactions in the quinoneimine + hydroquinone systems should be treated as a new class of liquid-phase reactions, as reversible chain processes. This was done for the example of the reaction between N-phenyl-1,4-benzoquinonemonoimine (QMI) and 2,5-dichlorohydroquinone $Ar(OH)_2$. The initial substances are not spent completely in such reactions but only up to the attainment of equilibrium with the reverse reaction between the products (4-hydroxydiphenylamine (H₂QMI) and 2,5-dichloroquinone (Q)). As for one-stage reversible reactions, the position of equilibrium in reversible chain reactions is independent of whether it is attained from the side of initial compounds or products. The equilibrium constant is also independent of the initial reagent concentrations and the presence of product admixtures but is only determined by the temperature. The fundamental special feature of reversible chain reactions is, however, the chain mechanism of both the forward and back reactions. The equilibrium state can therefore be attained as chain propagation from the side of either initial substances or products.

A kinetic analysis of reversible chain reactions in quinoneimine-hydroquinone systems was performed in [4]. An equation for the initial rate was obtained, which allowed a systematic study of the kinetics of these reactions to be performed and the rate constants for elementary steps to be determined from the experimental data. We undertook such a study for the chain reaction specified above. The results obtained for the forward reaction between N-phenyl-1,4-benzoquinomonoimine (QMI) and 2,5-dichlorohydroquinone $Ar(OH)_2$ were reported in [5]. The purpose of this work was to study the kinetics of the reverse chain reaction between 2,5-dichloroquinone (Q) and 4-hydroxydiphenylamine (H₂QMI), find a new independent set of elementary step rate constants, including those that we were unable to determine earlier, and compare the new data with those obtained earlier.

EXPERIMENTAL

2,5-Dichloroquinone Q from Aldrich was purified by double sublimation in a vacuum. 4-Hydroxydiphenylamine H₂QMI was recrystallized first from methanol and then from a heptane-toluene mixture. Finally, it was purified by preparative liquid chromatography on SiO_2 (Chemapol) with a mixture of ether and hexane as an eluent. 2,5-Dichlorohydroquinone $Ar(OH)_2$ was synthesized from Q by the reduction of the latter with sodium dithionite $Na_2S_2O_4$ following the procedure described in [6]. The product was purified by two-fold recrystalliziation from a methanol-benzene mixture. N-Phenyl-1,4-benzoquinonemonoimine QMI was synthesized by the oxidation of H_2QMI with PbO₂. It was finally purified by preparative liquid chromatography with an ether-hexane mixture as an eluent and recrystallized from methanol. We used tetraphenylhydrazine Ph₂N-NPh₂ as an initiator synthesized according to Wieland by the oxidation of diphenylamine in acetone with potassium permanganate KMnO₄ [7]. The rate constant for initiation with this initiator was $k_i = 2ek_{dec}$, where e = 0.95 is the probability of the escape of Ph₂N[•] radicals into volume and $k_{dec} = 2.06 \times 10^{-7} \text{ s}^{-1}$ is the rate constant for the decomposition of Ph₂N-NPh₂ in chlorobenzene at 298.2 K [3]. Chlorobenzene thoroughly purified from impurities as described in [8] was used as a solvent.

The reaction was monitored spectrophotometrically by tracking the accumulation of orange quinoneimine QMI. The reaction kinetics was studied at 298.2 ± 0.1 K in a temperature-controlled quartz cell of the bubbling reactor type (volume 8.5 ml, optical path l = 2.0 cm, bubbling of argon) mounted in a Specord UV VIS spectrophotometer. During experiments, we continuously recorded optical density changes for the QMI absorption band at v = const = 22260, 20000, or 19000 cm⁻¹ depending on the concentrations of the initial reagents and the amount of QMI introduced. 2,5-Dichloroquinone Q also absorbed weakly in this spectral region; the corresponding corrections were introduced.

The quantitative characteristics of the reaction of Q with H_2QMI were studied on the basis of the initial quinoneimine accumulation rates. The w_{QMI} values were determined by processing the initial experimental curve portions according to the empirical equation

$$[QMI] = a(1 + bexp(-ct))$$

where *a*, *b*, and *c* are the parameters selected iteratively. According to this equation, $w_{\text{OMI}} = -abc$.

RESULTS AND DISCUSSION

The reaction between Q and H_2QMI is the reverse reaction with respect to the reaction between QMI and



Fig. 1. Kinetic curves of (1, l', l'') consumption of QMI in the forward reaction between QMI and Ar(OH)₂ ([QMI]₀ = [Ar(OH)₂]₀ = 2 × 10⁻⁴ mol/1) and (2, 2', 2'') accumulation of QMI in the back reaction between Q and H₂QMI ([Q]₀ = [H₂QMI]₀ = 2 × 10⁻⁴ mol/1) and acceleration of the forward and back reactions in the presence of tetraphenylhydrazine $(w_i \times 10^{10}, \text{mol/(1 s)})$: (1, 2) 0, (1', 2') 1.17, and (1'', 2'') 7.05. Chlorobenzene, 298.2 K, Ar bubbling.

 $Ar(OH)_2$ studied earlier [5]. The stoichiometric equation of both reactions can be written as



The kinetic curves of the consumption of QMI in its reaction with $Ar(OH)_2$ and the accumulation of QMI in the reverse reaction between Q and H₂ QMI obtained in experiments with equal concentrations of the reagents are plotted in Fig. 1. The accelerating action of the initiator on the forward and back reactions, which is evidence of their chain mechanism, is also shown in this figure.

The forward and back reactions have the same mechanism. To unify the numbering of elementary steps, we here use the numbering introduced in [5]. The mechanism of the reaction of Q with H_2QMI can be written in the form of the kinetic scheme

Scheme

Ph₂N-NPh₂ → Ph₂N[•]
$$\xrightarrow{\text{Ar(OH)}_2, [H_2QMI]}$$

Ar(OH)O[•][HQMI[•]], (*i*)

 $Q + H_2QMI \longleftrightarrow Ar(OH)O^{\bullet} + HQMI^{\bullet}, (-5, 5)$ $Q + HQMI^{\bullet} \longleftrightarrow Ar(OH)O^{\bullet} + QMI, (-2, 2)$ $Ar(OH)O^{\bullet} + H_2QMI \longleftrightarrow Ar(OH)_2 + HQMI^{\bullet}, (-3, 3)$ $HQMI^{\bullet} + HQMI^{\bullet} \longleftrightarrow QMI + H_2QMI, (4, -4)$ $HQMI^{\bullet} + Ar(OH)O^{\bullet} \longleftrightarrow QMI + Ar(OH)_2, (-1, 1)$ $\longleftrightarrow H_2QMI + Q, (5, -5)$ $Ar(OH)O^{\bullet} + Ar(OH)O^{\bullet} \longleftrightarrow Ar(OH)_2 + Q. (6, -6)$

In this scheme, $Ar(OH)O^{\bullet}$ denotes 2,5-dichloro-4hydroxyphenoxyl semiquinone radicals and HQMI[•], radicals formed from quinoneimine QMI (or 4-hydroxydiphenylamine H₂QMI) by the addition of the H atom

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to QMI (or by the detachment of the H atom from H_2 QMI). These can be both 4-hydoxydiphenylaminyl HO–C₆H₄–N[•]–C₆H₆ and 4-anilinophenoxyl [•]O–C₆H₄– NH–C₆H₆ radicals. For simplicity, we make no distinction between HQMI[•] radicals, although it is known that, at 298.2 K in chlorobenzene, the mole fraction of [•]O–C₆H₄–NH–C₆H₆ radicals during the reaction is 0.967, and the mole fraction of HO–C₆H₄–N[•]–C₆H₆ radicals is 0.033 [9].

In the absence of an initiator and products, chains at the initial stages are initiated in reaction (-5). The role of chain propagation reactions is played by reactions (-2) and (-3), and chain termination occurs in the disproportionation of semiquinone radicals, reactions (-1) and (4)-(6).

The equation for the initial reaction rate has the form [4]

$$w_{\text{QMI}} = \frac{1}{1+\mu} \{ (w_{-5} + w_{-6} + 0.5w_i)\mu - (w_1 + w_{-4}) \} + \frac{\mu k_{-2}[Q] - k_2[Q\text{MI}]}{(1+\mu)k_t^{1/2}} (w_1 + w_{-4} + w_{-5} + w_{-6} + 0.5w_i)^{1/2},$$

where $\mu = (k_2[QMI] + k_{-3}[H_2QMI])/k_{-2}[Q] + k_3[Ar(OH)_2])$ and w_j are the rates of the corresponding reactions in the Scheme. Equation (1) was obtained on the assumption that the rate constants for the radical disproportionation reactions were approximately equal $(k_{-1} \approx k_4 \approx k_5 \approx k_6 \approx k_t)$.

Equation (1) contains two terms. The first term describes the accumulation of QMI at the chain initiation stage, and the second term is the rate of the accumulation of QMI in the chain reaction. If chains are fairly long, the first term can be ignored. The equation for the initial reaction rate then takes the form

$$w_{\rm QMI} = \frac{k_2 k_3 [Q] [H_2 QMI]}{k_t^{1/2} (k_2 [QMI] + k_{-3} [H_2 QMI] + k_{-2} [Q] + k_3 [Ar(OH)_2])} \times \left(\frac{k_{-2} k_{-3}}{k_2 k_3} - \frac{[QMI] [Ar(OH)_2]}{[Q] [H_2 QMI]}\right) (w_1 + w_{-4} + w_{-5} + w_{-6} + 0.5 w_i)^{1/2}.$$
(2)

Initiator Effects on the Initial Reaction Rate

According to (2), we have

$$w_{\text{QMI}} = \frac{k_{-2}k_{-3}[Q][\text{H}_{2}\text{QMI}]}{k_{t}^{1/2}(k_{-2}[Q] + k_{-3}[\text{H}_{2}\text{QMI}])} \times (k_{-5}[Q][\text{H}_{2}\text{QMI}] + 0.5w_{i})^{1/2}$$

in the presence of an initiator. The equation can more conveniently be verified experimentally in the form

$$w_{\text{QMI}}^{2} = \left\{ \frac{k_{-2}k_{-3}[Q][\text{H}_{2}\text{QMI}]}{k_{t}^{1/2}(k_{-2}[Q] + k_{-3}[\text{H}_{2}\text{QMI}])} \right\}^{2} \\ \times k_{-5}[Q][\text{H}_{2}\text{QMI}] \\ + 0.5 \left\{ \frac{k_{-2}k_{-3}[Q][\text{H}_{2}\text{QMI}]}{k_{t}^{1/2}(k_{-2}[Q] + k_{-3}[\text{H}_{2}\text{QMI}])} \right\}^{2} w_{i}.$$
(3)

According to (3), linear dependences should be observed in the $w_{\text{OMI}}^2 - w_i$ coordinates,

$$w_{\rm QMI}^2 = A + Bw_i. \tag{3a}$$

The ratio between the *y*-intercepts of these straight lines (*A*) and their slopes (*B*) is $2k_{-5}[Q][H_2QMI]$, which can be used to determine k_{-5} if $[Q]_0$ and $[H_2QMI]_0$ are known. The results obtained for the reaction in the presence of an initiator are shown in Fig. 2, and the *A* and *B* parameter values and the k_{-5} values found from their ratios are listed in Table 1.

We see that experiments in the presence of an initiator only allow us to obtain a crude estimate of $k_{-5} \sim (3.1 - 13.5) \times 10^{-3} \text{ l/(mol s)}$. Note that attempts at determining k_1 from the initiator effects on the rate of the forward reaction between QMI and Ar(OH)₂ also give crude estimates of k_1 only [4].

The Dependence of the Initial Reaction Rate on Reagent Concentrations

The results obtained in studying the dependence of w_{QMI} on the concentration of one of the reagents at a constant concentration of the other component are shown in Figs. 3 and 4. These dependences are nonlinear. Using (2), we obtain an equation that describes them. This equation has the form

$$w_{\rm QMI} = \frac{k_{-5}^{1/2} k_{-2} k_{-3} [Q]^{3/2} [H_2 QMI]^{3/2}}{k_t^{1/2} (k_{-2} [Q] + k_{-3} [H_2 QMI])}.$$
 (4)



Fig. 2. Dependences of the square of the initial reaction rate on the rate of initiation. Initial concentrations of Q $(\times 10^4)$ and H₂QMI $(\times 10^4)$, mol/1: (1) 2.0 and 2.0, (2) 4.0 and 2.0, and (3) 10.0 and 2.0, respectively. Chlorobenzene, 298.2 K.

The data presented in Figs. 3 and 4 lead us to conclude that $k_{-3} > k_{-2}$. Indeed, if we assume that, in the limiting case, $k_{-3} \gg k_{-2}$, we obtain $k_{-2}[Q] + k_{-3}[H_2QMI] \approx k_{-3}[H_2QMI]$. Equation (4) can then be written as

$$w_{\text{QMI}} \approx \frac{k_{-5}^{1/2} k_{-2}}{k_{t}^{1/2}} [Q]^{3/2} [H_2 \text{QMI}]^{1/2}.$$

It follows from this approximate equality that, at $[H_2QMI]_0 = \text{const}$, the rate of the reaction is $w_{QMI} \approx \text{const}_1[Q]^{3/2}$, and, at $[Q]_0 = \text{const}$, it is $w_{QMI} \approx \text{const}_2[H_2QMI]^{1/2}$. This is in qualitative agreement with the data shown in Figs. 3 and 4.

These data can be processed iteratively according to (4), which makes it possible in principle to determine three rate constants k_{-5} , k_{-2} , and k_{-3} simultaneously. This problem, however, does not have a unique solution, and the difference between the values of the same rate constant can be as large as several orders of magnitude. Additional independent data on k_{-5} , k_{-2} , and k_{-3} and



Fig. 3. Dependences of w_{QMI} on the concentration of H₂QMI at $[Q]_0 = \text{const} (\times 10^4, \text{mol/I}) = (1) 2.0, (2) 4.0, (3) 6.0, and (4) 10.0. The experimental data are shown by symbols. Lines correspond to calculations according to (4) with <math>k_{-5} = 1.5 \times 10^{-3}$ l/(mol s) and $k_{-2} \times 10^{-5}$ and $k_{-3} \times 10^{-6}$, l/(mol s), of (1) 6.1 and 3.2, (2) 6.4 and 3.5, (3) 5.2 and 5.4, and (4) 4.3 and 6.6, respectively. Chlorobenzene, 298.2 K.

their relative values were obtained in experiments with equal reagent concentrations.

The Reaction Rate at Equimolar Reagent and Product Concentrations (the Method of Equal Concentrations)

According to (2), the reaction rate in experiments with equimolar reagent concentrations $[Q]_0 = [H_2QMI]_0 = c$ is

$$w_{\rm QMI} = \left(\frac{k_{-5}}{k_t}\right)^{1/2} \frac{k_{-2}k_{-3}}{k_{-2} + k_{-3}} c^2 = \alpha c^2.$$
(5)

The dependence

$$w_{\rm QMI} = \left(\frac{k_{-5} + k_{-4}}{k_t}\right)^{1/2} \frac{k_{-2}k_{-3}}{k_{-2} + k_{-3} + k_2} c^2 = \beta c^2 \quad (6)$$

should hold in a series of experiments with the addition of the QMI product but equal concentrations of three substances, $[Q]_0 = [H_2QMI]_0 = [QMI]_0 = c$. For experi-

Table 1. Reaction characteristics in the presence of the initiator

| $[\text{H}_2\text{QMI}] \times 10^4,$ mol/l | $[Q] \times 10^4,$ mol/l | $\begin{array}{c} A,\\ (\text{mol}/(1\text{ s}))^2 \end{array}$ | <i>B</i> , mol/(1 s) | $k_{-5} \times 10^3,$ l/(mol s) |
|--|--------------------------|---|---------------------------------|------------------------------------|
| 2.0 | 2.0 | $(6.3 \pm 1.1) \times 10^{-16}$ | $(1.7 \pm 0.25) \times 10^{-6}$ | 4.6 ± 1.5 |
| 2.0 | 4.0 | $(5.0 \pm 1.7) \times 10^{-15}$ | $(3.6 \pm 1.0) \times 10^{-6}$ | 8.5 ± 5.0 |
| 2.0 | 10.0 | $(4.3 \pm 0.5) \times 10^{-14}$ | $(1.6 \pm 0.4) \times 10^{-5}$ | 6.6 ± 2.5 |

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Fig. 4. Dependences of w_{QMI} on the concentration of Q at $[\text{H}_2\text{QMI}]_0 = \text{const} (\times 10^4, \text{mol/l}) = (1) 2.0, (2) 4.0, (3) 6.0,$ and (4) 10.0. The experimental data are shown by symbols. Lines correspond to calculations according to (4) with $k_{-5} = 1.5 \times 10^{-3} \text{ l/(mol s)}$ and $k_{-2} \times 10^{-5}$ and $k_{-3} \times 10^{-6}$, l/(mol s), of (1) 6.5 and 4.4, (2) 6.6 and 2.0, (3) 5.8 and 2.2, and (4) 6.0 and 3.2, respectively. Chlorobenzene, 298.2 K.

ments with the addition of $Ar(OH)_2$ at $[Q]_0 = [H_2QMI]_0 = [Ar(OH)_2]_0 = c$, Eq. (2) yields a similar dependence,

$$w_{\text{QMI}} = \left(\frac{k_{-5} + k_{-6}}{k_t}\right)^{1/2} \frac{k_{-2}k_{-3}}{k_{-2} + k_{-3} + k_3} c^2 = \gamma c^2.$$
(7)

The results obtained at equal concentrations are shown in Fig. 5. We see that dependences (5)–(7) are close to linear in all cases. The data presented in Fig. 5 were processed to obtain the following parameters for Eqs. (5)–(7) (l/(mol s)): $\alpha = 0.567 \pm 0.025$ (curve *1*, no addition), $\beta = 0.649 \pm 0.041$ (curve *2*, addition of QMI), and $\gamma = 0.526 \pm 0.011$ (curve *3*, addition of Ar(OH)₂).

These values allow us to obtain initial rate constant estimates for several elementary reactions. These estimates can, in turn, be used as first approximations in the search for more exact constant values by iteration methods on the basis of other experimental data.

In particular, dividing the parameter of Eq. (6) by the parameter of Eq. (5) yields

$$\left(\frac{k_{-5}+k_{-4}}{k_{-5}}\right)^{1/2}\frac{k_{-2}+k_{-3}}{k_{-2}+k_{-3}+k_{2}} = 1.15 \pm 0.12.$$
(8)

Several points should be mentioned. Reactions (–4) and (–5) (see Scheme) are the transfer of the H atom from H₂QMI to QMI and from H₂QMI to Q, respectively. The 4-hydroxydiphenylamine molecule H₂QMI contains two reaction centers, the OH and NH bonds, and the dissociation energies of these bonds differ fairly substantially, $D_{\rm OH} = 339.3$ and $D_{\rm NH} = 353.4$ kJ/mol [10]. These data lead us to conclude that the more reac-



Fig. 5. Linear dependences of the rate of accumulation of QMI w_{QMI} on the square of equal reagent and product concentrations; (1) $[Q]_0 = [H_2QMI]_0 = c$, (2) $[Q]_0 = [H_2QMI]_0 = [Ar(OH)_2]_0 = c$, and (3) $[Q]_0 = [H_2QMI]_0 = [QMI]_0 = c$. Chlorobenzene, 298.2 K, Ar bubbling.

tive phenoxyl OH group of H₂QMI is predominantly involved in the reactions with QMI and Q. The QMI molecule also contains two reaction centers, the O and N atoms. If QMI attaches H at its O atom, the 4-hydroxydiphenylaminyl radical HQMI[•] with $D_{OH} = 259.5$ kJ/mol [10] is formed. The reaction of QMI at nitrogen yields the 4-anilinophenoxyl radical HQMI[•] with $D_{\rm NH}$ = 273.6 kJ/mol [10]. It follows that we mainly observe the second reaction, and the enthalpy of reaction (-4) is ΔH_{4} = 65.7 kJ/mol. The dissociation energy for the H–O bond of the Ar(OH)O[•] radical formed in reaction (-5) between Q and H_2QMI is $D_{OH} = 253.6$ kJ/mol [8]; that is, $\Delta H_{-5} = 85.7$ kJ/mol. It follows from the ΔH_{-4} and ΔH_{-5} values that $k_{-4} > k_{-5}$, even though Q contains two equivalent O atoms. Using this inequality and the $k_{-3} \gg k_{-2}$ inequality obtained above in (8) yields

$$\left(\frac{k_{-4}}{k_{-5}}\right)^{1/2} \frac{k_{-3}}{k_{-3}+k_2} \sim 1.15.$$
(9)

The assumption that $2k_i = 8 \times 10^8$ l/(mol s) (this is the mean rate constant for the disproportionation of semiquinone radicals [11, 12]) and the inequality $k_{-3} \gg k_{-2}$ allow us to obtain

$$k_{-5}^{1/2} k_{-2} \sim 1.2 \times 104 \; (l/(mol s))^{3/2}$$
 (10)

from the parameter of Eq. (5).

Multiplying (9) by (10) and substituting the value $k_{-4} = 6.4 \times 10^{-3} \text{ l/(mol s)}$ [3] into the result yields

$$\frac{k_{-2}}{1+k_2/k_{-3}} \sim 1.7 \times 10^5 \ \text{l/(mol s)}.$$
 (11)

Equation (11) allows us to estimate k_{-2} . For this purpose, let us compare the k_2 and k_{-3} rate constants using the heat effects of these reactions. In reaction (2), QMI attacks the Ar(OH)O[•] semiquinone radical at the OH bond ($D_{OH} = 253.6 \text{ kJ/mol} [8]$) with its N or O atom. This results in the formation of the HN ($D_{\rm NH} = 273.6 \text{ kJ/mol} [10]$) or OH ($D_{\rm OH} = 259.5 \text{ kJ/mol} [10]$) bond in the HQMI[•] radical. The heat effects of the first and second reactions are $\Delta H = -20$ and -5.9 kJ/mol, respectively. It follows that the first reaction should predominantly occur. In reaction (-3), the Ar(OH)O[•] radical attacks the H₂QMI molecule at its H-O or H-N group. The dissociation energies of these groups are $D_{\text{OH}} = 339.3 \text{ and } D_{\text{NH}} = 353.4 \text{ kJ/mol} [10]. The strength of the resulting HO bond in Ar(OH)₂ is <math>D_{\text{OH}} = 362.4 \text{ kJ/mol} [8].$ The enthalpies of the reactions with the attack at the HO and NH groups are $\Delta H = -23.1$ and -9 kJ/mol; that is, the first reaction predominates. The close heat effect values for reactions (2) and (-3) lead us to suggest that $k_2 \approx k_{-3}$. Equation (11) then gives the estimate

$$k_{-2} \sim 3.4 \times 10^5 \, \text{l/(mol s)}.$$
 (12)

Accordingly, we find from (10) that

$$k_{-5} \sim 1.2 \times 10^{-3} \, \text{l/(mol s)}.$$
 (13)

Lastly, let us estimate k_{-6} . Let us divide the parameter of (7) by the parameter of (5),

$$\left(\frac{k_{-5}+k_{-6}}{k_{-5}}\right)^{1/2}\frac{k_{-2}+k_{-3}}{k_{-2}+k_{-3}+k_{3}}=0.93.$$

The equilibrium constant K of the reaction between Q and H₂QMI equals the product $K = K_{-2}K_{-3} = (k_{-2}/k_2) \times$ (k_{-3}/k_3) [4] and is close to one (K = 3.2) [1, 8] (see Fig. 1). For this reason, if $k_2 \approx k_{-3}$ and $k_{-3} \gg k_{-2}$ (see above), we have $k_{-2} \approx k_3 \ll k_{-3}$. The last equation therefore gives

 $\left(\frac{k_{-5}+k_{-6}}{k_{-5}}\right)^{1/2} \approx 0.93$

and

$$k_{-6} \approx 0.13 k_{-5} \sim 1.6 \times 10^{-4} \, \text{l/(mol s)}.$$
 (14)

Calculation of Reaction Rate Constants k_{-5} , k_{-2} , and k_{-3} from the Dependence of the Reaction Rate on the Concentration of the Initial Substances

We iteratively processed the data shown in Figs. 3 and 4 according to (4) taking into account estimates (5)-(14). Two parameters, k_{-2} and k_{-3} , were adjusted at a fixed k_{-5} value. The latter was varied over the range $(0.5-5) \times 10^{-3}$ l/(mol s) in steps of 5×10^{-4} l/(mol s). A comparison of the data obtained showed that the results were in the closest agreement with each other and in satisfactory agreement with estimates (5)–(14) at k_{-5} = $(1.5 \pm 0.5) \times 10^{-3}$ l/(mol s). The k_{-2} and k_{-3} values obtained in each series of experiments at this k_{-5} value are given in the captions to Figs. 3 and 4.

mol/l): (1) 6.0 and 6.0, (2) 12.0 and 4.0, and (3) 4.0 and 12.0, respectively. The experimental data are shown by

symbols. Lines correspond to calculations according to (15) with $k_{-5} = 1.5 \times 10^{-3}$ l/(mol s) and $k_{-4} = 6.4 \times 10^{-3}$ l/(mol s); $k_2 \times 10^{-6}$, $k_{-2} \times 10^{-5}$, and $k_{-3} \times 10^{-6}$ values (l/(mol s)): (1) 2.9, 8.1, and 2.1; (2) 3.0, 5.1, and 2.2; and (3) 3.3, 7.1, and 1.2, respectively. Chlorobenzene, 298.2 K, Ar bubbling.

On the whole, studies of the dependence of the initial reaction rate on reagent concentrations gave (k, 1/(mol s))

$$k_{-5} = (1.5 \pm 0.5) \times 10^{-3}, \quad k_{-2} = (5.9 \pm 0.3) \times 10^{5},$$

 $k_{-3} = (3.8 \pm 0.6) \times 10^{6}.$

The Influence of Products on the Initial Reaction Rate

The Dependence of the Reaction Rate on the Concentration of Quinonemonoimine QMI

The addition of QMI in small amounts increases the initial reaction rate w_{OMI}, although, clearly, equilibrium shifts to the initial substances in the presence of QMI, and, seemingly, the rate of the reaction should decrease. These data are evidence of a complex mechanism of the reaction between Q and H₂QMI.

Figure 6 shows that the dependences of $w_{\rm OMI}$ on [QMI]₀ are curves with maxima, whose positions depend on the ratio between the concentrations of Q and H₂QMI. We observed similar dependences in studying the influence of H₂QMI on the rate of the forward reaction between QMI and Ar(OH)₂ [5]. The dual character of the action of QMI (accelerating and decelerating) is explained by its participation in reactions that have opposite effects on the rate of the overall process. In the presence of QMI, additional initiation reac-

2.8 2 2.4 2.08 4 $[QMI] \times 10^4$, mol/l Fig. 6. Dependences of the initial rate of the reaction between Q and H₂QMI on the concentration of the reaction product QMI. Initial concentrations of Q and H₂QMI (×10⁴





Fig. 7. Dependences of the initial rate of the reaction between Q and H₂QMI on the concentration of Ar(OH)₂. Initial concentrations of Q and H₂QMI (×10⁴, mol/l): (*I*) 6.0 and 6.0, (2) 4.0 and 6.0, (3) 4.0 and 12.0, and (4) 12.0 and 4.0, respectively. The experimental data are shown by symbols. Lines correspond to iterative calculations according to (16) with $k_{-5} = 1.5 \times 10^{-3}$ l/(mol s); $k_3 \times 10^{-5}$, $k_{-2} \times 10^{-5}$, $k_{-3} \times 10^{-6}$, and $k_{-6} \times 10^4$ values (l/(mol s)): (*I*) 3.3, 4.4, 2.7, and 1.6; (2) 5.6, 5.2, 4.0, and 5.0; (3) 3.3, 5.2, 1.9, and 1.0; and (4) 1.6, 7.4, 1.1, and 1.5, respectively. Chlorobenzene, 298.2 K.

tion (-4) initially occurs in the system. This increases the rate of the chain reaction between Q and H₂QMI. Simultaneously, the rate of reaction (2) becomes increasingly higher as the concentration of QMI increases, which decreases the chain length and the rate of the reaction. Equation (2) can be used to determine the rate of the reaction in the presence of QMI,

$$w_{\text{QMI}} = \frac{k_{-2}k_{-3}[Q][H_2QMI]^{3/2}}{k_t^{1/2}(k_{-2}[Q] + k_{-3}[H_2QMI] + k_2[QMI])} (15) \times (k_{-5}[Q] + k_{-4}[QMI])^{1/2}.$$

We used (15) and the $k_{-4} = 6.4 \times 10^{-3}$ l/(mol s) value obtained in [3] to iteratively process the experimental data shown in Fig. 6. For each curve, three parameters $(k_2, k_{-2}, \text{ and } k_{-3})$ were determined at a fixed k_{-5} value; k_{-5} was varied over the range $(0.5-5) \times 10^{-3}$ l/(mol s) in steps of 5×10^{-4} l/(mol s). A comparison of the results obtained this way showed that $k_{-5} = 1.5 \times 10^{-3}$ l/(mol s) again gave the closest agreement. The k_2 , k_{-2} , and k_{-3} values obtained in each series of experiments at $k_{-4} = 6.4 \times 10^{-3}$ and $k_{-5} = 1.5 \times 10^{-3}$ l/(mol s) are given in the caption to Fig. 6.

Our study of the dependence of w_{QMI} on the concentration of QMI gave the following results (k, l/(mol s)):

$$k_{-5} = 1.5 \times 10^{-3}, \quad k_2 = (3.1 \pm 0.2) \times 10^6,$$

 $k_3 = (6.8 \pm 0.9) \times 10^5, \quad k_3 = (1.8 \pm 0.3) \times 10^6.$

The Dependence of the Rate of the Reaction on the Concentration of 2,5-Dichlorohydroquinone Ar(OH)₂

Figure 7 shows that the addition of $Ar(OH)_2$ has a weak inhibiting action on the reaction of Q with H₂QMI. Note that we observed a similar effect of the addition of Q for the forward reaction between QMI and $Ar(OH)_2$ [5]. Equation (2) yields the rate of the reaction in the presence of $Ar(OH)_2$ in the form

$$w_{\rm QMI} = \frac{k_{-2}k_{-3}[Q]^{3/2}[H_2QMI]}{k_t^{1/2}(k_{-2}[Q] + k_{-3}[H_2QMI] + k_3[Ar(OH)_2])} (k_{-5}[Q] + k_{-6}[Ar(OH)_2])^{1/2}.$$
 (16)

Equation (16) is similar to (15) for the dependence of w_{QMI} on the concentration of QMI, but the curves in Figs. 6 and 7 have different shapes, which is evidence that $k_{-4}[\text{QMI}] \gg k_{-6}[\text{Ar}(\text{OH})_2]$ at close concentrations of QMI and $\text{Ar}(\text{OH})_2$; that is, $k_{-4} \gg k_{-6}$. The data presented in Fig. 7 were used to estimate k_3 and k_{-6} by the method of iterations. The k_{-5} constant was set at a constant value, $k_{-5} = 1.5 \times 10^{-3} \text{ l/(mol s)}$, and k_{-3} and k_{-2} were varied over the ranges $(1-5) \times 10^6$ and $(4-9) \times 10^5 \text{ l/(mol s)}$, respectively. The k values obtained are given in the caption to Fig. 7.

On the whole, our study of the dependence of w_{QMI} on the concentration of H₂QMI gave the following results (*k*, l/(mol s)):

$$k_3 = (3.4 \pm 0.8) \times 10^5$$
, $k_{-2} = (5.6 \pm 0.7) \times 10^5$,

$$k_{-3} = (2.4 \pm 0.6) \times 10^6, \quad k_{-6} = (2.2 \pm 0.9) \times 10^{-4}.$$

A comparison of the sets of k values given above leads us to conclude that the estimates obtained for the rate constants of the same elementary steps satisfactorily agree with each other irrespective of the method used for their determination. Table 2 presents the averaged values of the reaction rate constants for the elementary steps. For comparison, the results obtained in [5] for the back chain reaction between QMI and Ar(OH)₂ are also included (Table 2).

A comparison of the data obtained in this work and [5] shows that the results of these two independent studies augment each other, and the estimates of the rate constants of the same elementary reactions are closely similar.

Table 2. Rate constants $(k_{298}, 1/(\text{mol s}))$ of the elementary steps obtained in [5] and this work for the reversible chain reaction between QMI and Ar(OH)₂

| Stage | Back reaction $Q + H_2QMI$ | Forward reaction $QMI + Ar(OH)_2$ [5] | |
|---------|--|---|--|
| (1, -1) | $k_1 = ?$ | $k_1 = (3.5 \pm 1) \times 10^{-4}$ | |
| | $2k_{-1} = 8 \times 10^8$ | | |
| (2, -2) | $k_2 = (3.1 \pm 0.2) \times 10^6$ | $k_2 = (1.8 \pm 0.7) \times 10^6$ | |
| | $k_{-2} = (6.3 \pm 1.3) \times 10^5$ | $k_{-2} = (6 \pm 2.5) \times 10^5$ | |
| (3, -3) | $k_3 = (3.4 \pm 0.8) \times 10^5$ | $k_3 = (2.4 \pm 0.6) \times 10^5$ | |
| | $k_{-3} = (2.7 \pm 1) \times 10^6$ | $k_{-3} = (2.3 \pm 0.3) \times 10^6$ | |
| (4, -4) | $2k_4 = 8 \times 10^8$ | | |
| | $k_{-4} = 6.4 \times 10^{-3} [3]$ | | |
| (5, -5) | $2k_5 = 8 \times 10^8$ | | |
| | $k_{-5} = (1.5 \pm 0.5) \times 10^{-3} k_{-5} = ?$ | | |
| (-1, 1) | $2k_{-1} = 8 \times 10^8$ | | |
| | $k_1 = ?$ | $k_1 = (3.5 \pm 1) \times 10^{-4}$ | |
| (6, -6) | $2k_6 = 8 \times 10^8$ | | |
| | $k_{-6} = (2.2 \pm 0.9) \times 10^{-4}$ | $k_{-6} = (0.8 \pm 0.4) \times 10^{-4}$ | |

To summarize, our study of the kinetics of the forward and back chain "half-reactions" allowed us to characterize all the elementary reactions of the overall reversible chain reaction in the quinoneimine + hydroquinone system for the first time and obtain reliable estimates of their rate constants. The results substantiated the mechanism of such reactions suggested earlier and the validity of the equations obtained in a kinetic analysis of this mechanism. We also suggested procedures for experimental data processing.

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