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Rate constants of elementary steps of the reversible chain reaction of *N*-phenyl-1,4-benzoquinonemonoimine with 2,5-dichlorohydroquinone

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The kinetics of reversible chain reactions in quinoneimine—hydroquinone systems has first been studied for the reaction of *N*-phenyl-1,4-benzoquinonemonoimine with 2,5-dichlorohydroquinone used as an example. The dependences of the reaction rate on the concentration of the initial reactants, initiator, and each product were studied. The reliable estimates of the rate constants of 11 (of 12) elementary steps of this reaction were obtained from the experimental data using the earlier derived formulas and the method of equal concentrations developed in the present work.

Key words: *N*-phenyl-1,4-benzoquinonemonoimine, 2,5-dichlorohydroquinone, semiquinone radicals, reversible chain reactions, kinetics, mechanism, elementary steps, reaction rate constants.

Quinoneimines are nitrogen analogs of quinones and, hence, the reactions of quinoneimines with hydroquinones are model in investigation of the interaction of quinones with hydroquinones. Therefore, the study of the kinetics and mechanism of reversible chain reactions in quinoneimine—hydroquinone systems is urgent for chemistry and biology, because facilitates understanding of the mechanism of action of lipid-soluble bioantioxidants of the quinone type (ubiquinones, vitamins K).[1]

The chain mechanism of the reactions in quinoneimines with hydroquinones was determined for the first time for the reaction of *N*-phenyl-1,4-benzoquinonemonoimine (**1**) with 2,5-di-*tert*-butylhydroquinone.[2,3] The study of the kinetics of this reaction in the presence of one of the products, *viz.*, 4-hydroxydiphenylamine (**2**), gave evidence that the reactions in the quinoneimine—hydroquinone systems is a reversible chain process.[4] This conclusion has recently[5] been confirmed experimentally for the reaction of quinoneimine **1** with 2,5-dichlorohydroquinone (**3**). The equation for the initial rate was derived from a kinetic analysis of the mechanism of these reversible chain reactions,[6] which enables the purposeful systematic study of the kinetic regularities of the reactions and determination of the rate constants of elementary steps from the experimental data. In the present work, such a study was carried out for the first time for the reaction of quinoneimine **1** with hydroquinone **3**.

Experimental

Compound **2** (analytically pure grade) was recrystallized from methanol and then from a heptane—toluene mixture, and the final purification was carried out by liquid chromatography on SiO_2 (Chemapol) using ether—hexane mixtures as eluent.

N-Phenyl-1,4-benzoquinonemonoimine (**1**) was synthesized by the oxidation of compound **2** using PbO_2 in a glass column (5×0.8 cm) packed with PbO_2 through which an ethereal solution of compound **2** was slowly passed. Sample **1** was purified by preparative LC on SiO_2 (ether—hexane mixture as eluent) and recrystallized from methanol.

2,5-Dichloroquinone (**4**, Aldrich) was purified by double sublimation *in vacuo*. A portion of purified sample **4** was used for the synthesis of hydroquinone **3** by the reduction of dichloroquinone **4** by $Na_2S_2O_4$ using an earlier described procedure,[7] and hydroquinone **3** was twice recrystallized from methanol.

The initiator tetraphenylhydrazine $Ph_2N—NPh_2$ (**5**) as the source of diphenylaminyl radicals $Ph_2N^{\bullet}$ ($\mathbf{5}^{\bullet}$) was synthesized according to the Wieland method by the oxidation of diphenylamine with $KMnO_4$ in acetone.[8] The initiation rate constant of this initiator is $k_i = 2ek_{\text{decomp}}$, where $e = 0.95$ is the probability of radicals $\mathbf{5}^{\bullet}$ escape into the bulk, and the rate constant of decomposition of initiator **5** in chlorobenzene at 298.2 K is $k_{\text{decomp}} = 2.06 \cdot 10^{-7}\ s^{-1}$.[3]

The criterion of purity of all reagents used was the absence or a negligible intensity of peaks of admixtures on the liquid chromatograms of the samples with UV detection at $\lambda = 290$ nm.

Chlorobenzene (Fluka) thoroughly purified from admixtures according to an earlier described procedure[9] was used as a solvent.

The reaction kinetics was studied at 298.2±0.1 K in a temperature-controlled quartz cell (reactor) of the bubbling type (volume 8.5 mL, optical path length $l = 2.0$ cm, argon bubbling) embedded in a Specord UV—Vis spectrophotometer. The absorbance at λ = const = 449.2, 500, or 526.3 nm (ν = 22260, 20000, or 19000 cm^{-1}), depending on the initial concentration of **1** was continuously detected during experiment. Dichloroquinone **4** also absorbed weakly in this region, which was taken into account by introduction of the corresponding corrections.

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The quantitative regularities of the reaction of compound **1** with **3** were studied by the initial rates of consumption of quinoneimine **1** (w_1). To determine the numerical w_1 values, the initial regions of the experimental curves were processed by the empirical equation

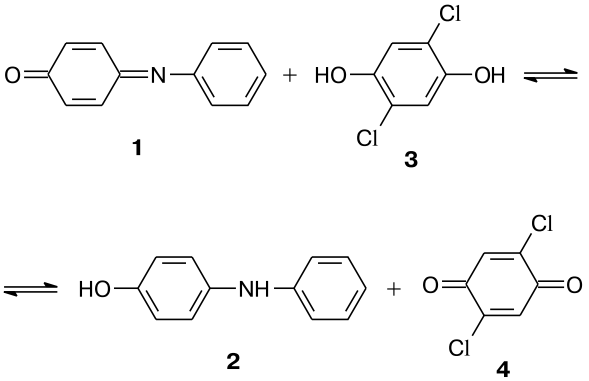
$$[\mathbf{1}] = a[1 - b\exp(-ct)],$$

where a, b, and c are the parameters chosen by an iteration method. In this case, $w_1 = abc$.

Results and Discussion

The stoichiometric equation for the reaction of compounds **1** and **3** are presented in Scheme 1.

Scheme 1



The kinetic curves of quinoneimine **1** consumption in the forward reaction with hydroquinone **3** and accumulation of **1** in the backward reaction of compounds **2** and **4** in experiments with equimolar concentrations of the reactants are shown in Fig. 1. The data show the accelerating effect of additives of initiator **5** on the forward and backward reactions, indicating the chain mechanism of the both reactions.

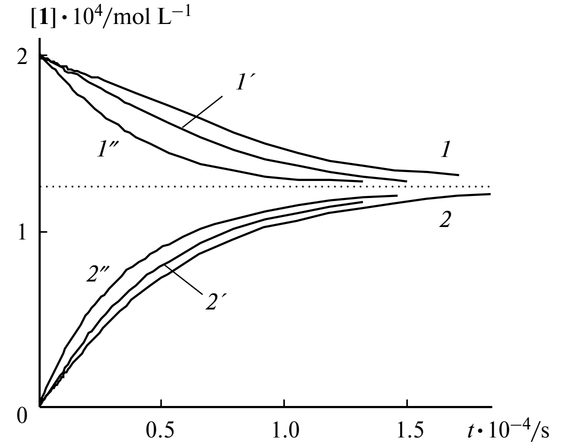


Fig. 1. Kinetic curves of consumption of quinoneimine **1** ($2\cdot10^{-4}$ mol L^{-1}) in the forward reaction with hydroquinone **3** ($2\cdot10^{-4}$ mol L^{-1}) (*1, 1′, 1″*) and accumulation of quinoneimine **1** in the backward reaction of **2** ($2\cdot10^{-4}$ mol L^{-1}) and **4** ($2\cdot10^{-4}$ mol L^{-1}) (*2, 2′, 2″*). Acceleration of the forward and backward reactions in the presence of initiator **5** with $w_i\cdot10^{10} = 0$ (*1, 2*); 1.17 (*1′, 2′*); 7.05 mol L^{-1} s^{-1} (*1″, 2″*). Chlorobenzene, 298.2 K, Ar bubbling.

The mechanism of the reaction of compounds **1** and **3** is presented as kinetic Scheme 2.[2,6]

Scheme 2

$$\mathbf{5} \longrightarrow \mathbf{5}^{\bullet} \xrightarrow{\mathbf{3},\ [\mathbf{2}]} \mathbf{5}_{\mathbf{H}} + \mathbf{6}^{\bullet}\ [\mathbf{7}^{\bullet}] \qquad \text{(i)}$$

$$\mathbf{1} + \mathbf{3} \rightleftharpoons \mathbf{7}^{\bullet} + \mathbf{6}^{\bullet} \qquad (1), (-1)$$

$$\mathbf{1} + \mathbf{6}^{\bullet} \rightleftharpoons \mathbf{7}^{\bullet} + \mathbf{4} \qquad (2), (-2)$$

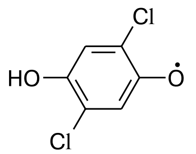
$$\mathbf{7}^{\bullet} + \mathbf{3} \rightleftharpoons \mathbf{2} + \mathbf{6}^{\bullet} \qquad (3), (-3)$$

$$\mathbf{7}^{\bullet} + \mathbf{7}^{\bullet} \rightleftharpoons \mathbf{1} + \mathbf{2} \qquad (4), (-4)$$

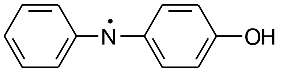
$$\mathbf{7}^{\bullet} + \mathbf{6}^{\bullet} \rightleftharpoons \mathbf{2} + \mathbf{4} \qquad (5), (-5)$$

$$\mathbf{6}^{\bullet} + \mathbf{6}^{\bullet} \rightleftharpoons \mathbf{3} + \mathbf{4} \qquad (6), (-6)$$

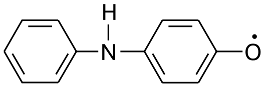
In this scheme, $\mathbf{5}_{\mathbf{H}}$ designates diphenylamine Ph_2NH, $\mathbf{6}^{\bullet}$ are 2,5-dichloro-4-hydroxyphenoxyl semiquinone radicals, and $\mathbf{7}^{\bullet}$ are radicals formed from quinoneimine **1** (or from 4-hydroxydiphenylamine **2**) by H atom addition to molecule **1** (or by H atom abstraction from molecule **2**). These can be both 4-hydroxydiphenylaminyl $\mathbf{7}_{\mathbf{N}}^{\bullet}$ and 4-anilinophenoxy radicals $\mathbf{7}_{\mathbf{O}}^{\bullet}$, the difference between which is not considered for simplicity.*



$\mathbf{6}^{\bullet}$



$\mathbf{7}_{\mathbf{N}}^{\bullet}$



$\mathbf{7}_{\mathbf{O}}^{\bullet}$

The equation for the initial reaction rate has the following form[6]:

$$w_1 = [1/(1+\lambda)][\lambda(w_1 + w_{-4}) - (w_{-5} + w_{-6} + 0.5w_i)] + \frac{\lambda k_2[\mathbf{1}] - k_{-2}[\mathbf{4}]}{(1+\lambda)k_t^{1/2}}\sqrt{w_1 + w_{-4} + w_{-5} + w_{-6} + 0.5w_i}, \qquad \text{(I)}$$

where $\lambda = (k_{-2}[\mathbf{4}] + k_3[\mathbf{3}])/(k_2[\mathbf{1}] + (k_{-3}[\mathbf{2}])$, and w_j are the rates of the corresponding steps in Scheme 2. Equa-

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* In chlorobenzene at $T = 298.2$ K the molar fraction of radicals $\mathbf{7}_{\mathbf{O}}^{\bullet}$ $x = 0.967$, and the molar fraction of radicals $\mathbf{7}_{\mathbf{N}}^{\bullet}$ is $1 - x = 0.033$.[10]

tion (I) was obtained under assumption that the disproportionation rate constants of the radicals differ slightly, *i.e.*, $k_4 \approx k_{-1} \approx k_5 \approx k_6 \approx k_t$.

Equation (I) contains two terms. The first of them takes into account the consumption of quinoneimine **1** in the steps of chain initiation and free radical formation, and the second term is equal to the rate of its consumption in the chain reaction. If the chains are rather long, the first term can be neglected. In this case, the expression for the initial reaction rate has the form

$$w_{\mathbf{1}} = \frac{k_{-2}k_{-3}[\mathbf{1}][\mathbf{3}]}{k_t^{1/2}\left(k_2[\mathbf{1}] + k_{-2}[\mathbf{4}] + k_3[\mathbf{3}] + k_{-3}[\mathbf{2}]\right)} \cdot$$

$$\cdot\left(\frac{k_2k_3}{k_{-2}k_{-3}} - \frac{[\mathbf{4}][\mathbf{2}]}{[\mathbf{1}][\mathbf{3}]}\right)\sqrt{w_1 + w_{-4} + w_{-5} + w_{-6} + 0.5w_i}\,. \qquad \text{(II)}$$

Effect of the initiator on the initial reaction rate. According to formula (II), in the presence of the initiator

$$w_{\mathbf{1}} = \frac{k_2k_3[\mathbf{1}][\mathbf{3}]}{k_t^{1/2}\left(k_2[\mathbf{1}] + k_3[\mathbf{3}]\right)}\sqrt{k_1[\mathbf{1}][\mathbf{3}] + 0.5w_i}$$

or in the form more suitable for experimental verification,

$$w_{\mathbf{1}}^2 = \left\{\frac{k_2k_3[\mathbf{1}][\mathbf{3}]}{k_t^{1/2}\left(k_2[\mathbf{1}] + k_3[\mathbf{3}]\right)}\right\}^2 k_1[\mathbf{1}][\mathbf{3}] +$$

$$+\ 0.5\left\{\frac{k_2k_3[\mathbf{1}][\mathbf{3}]}{k_t^{1/2}\left(k_2[\mathbf{1}] + k_3[\mathbf{3}]\right)}\right\}^2 w_i. \qquad \text{(III)}$$

According to Eq. (III), linear plots should be observed in the coordinates $w_{\mathbf{1}}^2$—w_i. The ratio of the sections cut in the ordinate to the slope ratio is $2k_1[\mathbf{1}][\mathbf{3}]$, from which k_1 can be determined at the known [**1**] and [**3**] values.

The results of studying the reaction in the presence of initiator **5** are presented in Figs 2 and 3. At low concentrations of compounds **1** and **3**, linear dependences of $w_{\mathbf{1}}^2$ on w_i are not fulfilled (see Fig. 2). With increasing $[\mathbf{3}]_0$, *i.e.*, when the equilibrium state shifts toward the products, the plots of $w_{\mathbf{1}}^2$ *vs.* w_i become closer to linear (see Fig. 2). To obtain quantitative results, the data in Figs 2 and 3 were approximated by the empirical function $w_{\mathbf{1}}^2 = a + b[1 - \exp(-cw_i)]$, according to which the intersept in the ordinate equals a and the slope ratio at $w_i \to 0$ is bc. The results obtained are given in Table 1.

It is seen that only a rough estimate of k_1 can be obtained from experiments in the presence of the initiator.

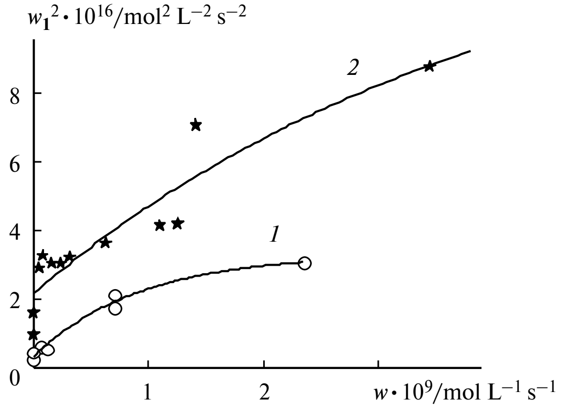

Fig. 2. Plots of $w_{\mathbf{1}}^2$ *vs.* w_i at low concentrations of compounds **1** ($\cdot 10^4$) and **3** ($\cdot 10^4$), mol L^{-1}: 2.0 and 2.0 (*1*); 2.0 and 4.0 (*2*), respectively. Chlorobenzene, 298.2 K, Ar bubbling.

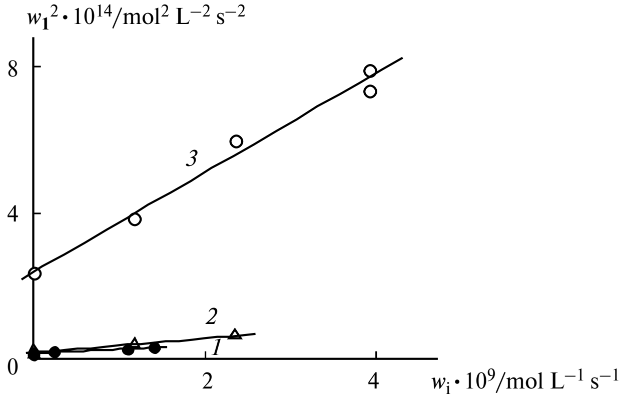

Fig. 3. Dependence of the squared initial reaction rate on the initiator concentration. Initial concentrations of compounds **1** ($\cdot 10^4$) and **3** ($\cdot 10^3$), mol L^{-1}: 2.0 and 1.0 (*1*); 2.0 and 1.2 (*2*); 10.0 and 1.2 (*3*), respectively.

Dependence of the initial reaction rate on the reactant concentrations. *Ratio between the reaction rate constants* k_2 *and* k_3. The results of studying the dependence of $w_{\mathbf{1}}$ on the concentration of one of the reactants at a constant concentration of another reactant are shown in Figs 4 and 5. They are nonlinear, and the humps of the curves $w_{\mathbf{1}} = f[\mathbf{1}]$ at $[\mathbf{3}]_0$ = const look up (see Fig. 4), while those of the curves $w_{\mathbf{1}} = f[\mathbf{3}]$ at $[\mathbf{1}]_0$ = const look down (see

Table 1. Results of approximation of the dependence of $w_{\mathbf{1}}^2$ on w_i by the empirical dependence $w_{\mathbf{1}}^2 = a + b[1 - \exp(-cw_i)]$

[**1**]	[**3**]	Cut section*	Slope**	k_1*** $\cdot 10^3$
10^4 mol L^{-1}				
2.0	2.0	$(3.5\pm1.0)\cdot10^{-17}$	$(3.2\pm1.5)\cdot10^{-7}$	1.4±1.0
2.0	4.0	$(2.2\pm0.4)\cdot10^{-16}$	$(2.8\pm2.1)\cdot10^{-7}$	4.9±4.5
2.0	10.0	$(1.6\pm0.12)\cdot10^{-15}$	$(1.2\pm0.2)\cdot10^{-6}$	3.3±0.8
2.0	12.0	$(1.9\pm0.3)\cdot10^{-15}$	$(1.9\pm0.3)\cdot10^{-6}$	2.1±0.7
2.0	36.0	$(1.8\pm0.1)\cdot10^{-14}$	$(3.2\pm0.4)\cdot10^{-6}$	4.0±1.5
10.0	12.0	$(2.4\pm0.3)\cdot10^{-14}$	$(1.4\pm0.1)\cdot10^{-5}$	0.7±0.14

* In mol^2 L^{-2} s^{-2}.
** In mol L^{-1} s^{-1}.
*** In L mol^{-1} s^{-1}.

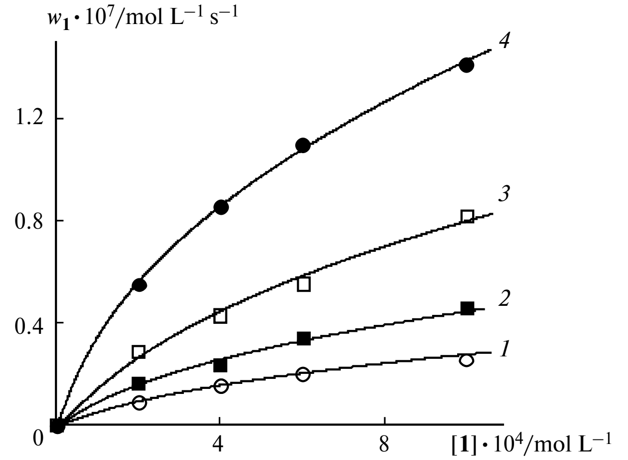

Fig. 4. Plots of w_1 *vs.* concentration of quinoneimine **1** at $[\mathbf{3}]_0$ = const (• 10^{-4}, mol L^{-1}): 2.0 (*1*); 4.0 (*2*); 6.0 (*3*); 10.0 (*4*). Points are experiment, and lines are calculation by formula (IV) at $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1} and the following $k_2 \cdot 10^{-6}$ and $k_3 \cdot 10^{-5}$ values, L mol^{-1} s^{-1}: 2.34 and 4.55 (*1*); 1.63 and 2.84 (*2*); 1.75 and 2.85 (*3*); 5.56 and 2.32 (*4*), respectively. Chlorobenzene, 298.2 K.

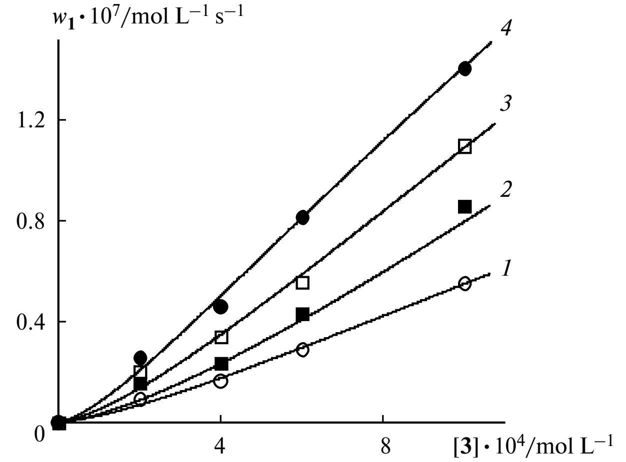

Fig. 5. Plots of w_1 *vs.* concentration of hydroquinone **3** at $[\mathbf{1}]_0$ = const (• 10^{-4}, mol L^{-1}): 2.0 (*1*); 4.0 (*2*); 6.0 (*3*); 10.0 (*4*). Points are experiment, and lines are calculation by formula (IV) at $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1} and the following $k_2 \cdot 10^{-6}$ and $k_3 \cdot 10^{-5}$ values, L mol^{-1} s^{-1}: 2.71 and 2.81 (*1*); 2.15 and 2.44 (*2*); 1.03 and 3.22 (*3*); 1.39 and 2.55 (*4*). Chlorobenzene, 298.2 K, Ar bubbling.

Fig. 5). Using Eq. (II), we have the formula to describe these dependences

$$w_1 = \frac{k_1^{1/2} k_2 k_3 [\mathbf{1}]^{3/2} [\mathbf{3}]^{3/2}}{k_t^{1/2} (k_2[\mathbf{1}] + k_3[\mathbf{3}])}. \qquad \text{(IV)}$$

Analysis of the data presented in Figs 4 and 5 (in the framework of Eq. (IV)) suggests that $k_2 > k_3$. Indeed, assuming in the extreme case that $k_2 \gg k_3$, we have $k_2[\mathbf{1}] + k_3[\mathbf{3}] \approx k_2[\mathbf{1}]$, and then Eq. (IV) can be written in the form

$$w_1 \approx (k_1^{1/2} k_3 / k_t^{1/2}) [\mathbf{1}]^{1/2} [\mathbf{3}]^{3/2}.$$

It is seen that at $[\mathbf{3}]_0$ = const the reaction rate $w_1 \approx \text{const}_1 \cdot [\mathbf{1}]^{1/2}$, and at $[\mathbf{1}]_0$ = const the reaction rate $w_1 \approx \text{const}_2 \cdot [\mathbf{3}]^{3/2}$. This agrees qualitatively with Figs 4 and 5.

Processing of the data (see Figs 4 and 5) by the iteration methods using Eq. (IV) makes it possible to determine simultaneously three reaction rate constants: k_1, k_2, and k_3. However, this problem has no unambiguous solution, and differences in the determined values of the same rate constant are several orders of magnitude. To obtain additional independent data on the k_1, k_2, and k_3 values and ratios between them, we used the results of experiments carried out at equal concentrations of the reactants.

Reaction rate at equimolar concentrations of reactants and products (equal concentrations method). According to Eq. (II), the reaction rate in experiments with equimolar reactant concentrations $[\mathbf{1}]_0 = [\mathbf{3}]_0 = c$ is the following:

$$w_1 = (k_1/k_t)^{1/2} [k_2 k_3 / (k_2 + k_3)] c^2. \qquad \text{(V)}$$

In the experimental series with additives of reaction product **2** but at equal concentrations of all the three substances $[\mathbf{1}]_0 = [\mathbf{3}]_0 = [\mathbf{2}]_0 = c$, the following dependence should obey:

$$w_1 = [(k_1 + k_{-4})/k_t]^{1/2} [k_2 k_3 / (k_2 + k_3 + k_{-3})] c^2. \qquad \text{(VI)}$$

In experiments with additives of quinone **4** at equal concentrations $[\mathbf{1}]_0 = [\mathbf{3}]_0 = [\mathbf{4}]_0 = c$, a similar dependence is obtained from Eq. (II)

$$w_1 = [(k_1 + k_{-6})/k_t]^{1/2} [k_2 k_3 / (k_2 + k_3 + k_{-2})] c^2. \qquad \text{(VII)}$$

The results of the experiments performed at equal concentrations are shown in Fig. 6. It can be seen that linear dependences (V)—(VII) obey well in all the cases. The data processing (see Fig. 6) gave the parameter values presented below.

Straight line in Fig. 6	Equation	Parameter	Value /L mol^{-1} s^{-1}
1	(V)	$\left(\frac{k_1}{k_t}\right)^{1/2} \frac{k_2 k_3}{k_2 + k_3}$	0.140±0.003
2	(VI)	$\left(\frac{k_1 + k_{-4}}{k_t}\right)^{1/2} \frac{k_2 k_3}{k_2 + k_3 + k_{-3}}$	0.218±0.011
3	(VII)	$\left(\frac{k_1 + k_{-6}}{k_t}\right)^{1/2} \frac{k_2 k_3}{k_2 + k_3 + k_{-2}}$	0.111±0.001

We used these results to estimate the rate constants of some elementary steps and then applied them as the first

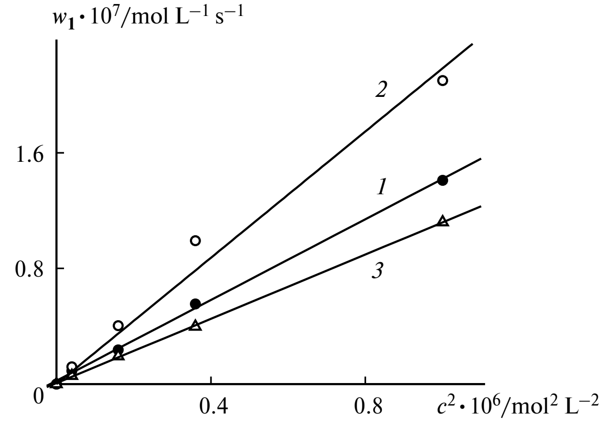

Fig. 6. Linear plots of the reaction rate w_1 *vs.* squared equal concentrations of the reactants and additives of the final products: *1*, $[\mathbf{1}]_0 = [\mathbf{3}]_0 = c$; *2*, $[\mathbf{1}]_0 = [\mathbf{3}]_0 = [\mathbf{2}]_0 = c$; *3*, $[\mathbf{1}]_0 = [\mathbf{3}]_0 = [\mathbf{4}]_0 = c$. Chlorobenzene, 298.2 K, Ar bubbling.

approximation in the search for their more exact values by the iteration method from other experimental data.

Dividing the parameter of Eq. (VI) into the parameter of Eq. (V), we have

$$\left(\frac{k_1 + k_{-4}}{k_1}\right)^{1/2} \frac{k_2 + k_3}{k_2 + k_3 + k_{-3}} = 1.56\pm0.11. \qquad \text{(VIII)}$$

According to Scheme 2, reactions (1) and (−4) are of the same type and represent H atom transfer to a molecule of **1** either from hydroquinone **3** (see reaction (1), two equal OH groups), or from compound **2** (see reaction (−4)). It follows from this that the reaction rate constants k_1 and k_{-4} are first determined by the strengths of the broken bonds in molecules **3** and **2**. The O—H bond dissociation energy in molecule **3** is known: D_{OH} = 362.4±0.9 kJ mol^{-1}.**[9]** In molecule **2** the O—H bond dissociation energy is much lower than that of the N—H bond: D_{NH} = 353.4 kJ mol^{-1}, D_{OH} = 339.3 kJ mol^{-1}.**[11]** It follows from the latter data that predominantly the phenoxy HO group of molecule **2** reacts with hydroquinone **1** in reaction (−4). Then, taking into account that D_{OH} in molecule **3** is considerably (by 23.1 kJ mol^{-1}) higher than D_{OH} в in molecule **2**, we conclude that $k_{-4} \gg k_1$.

Under an additional assumption that $k_2 \gg k_3$ (see above), it follows from Eq. (VIII)

$$(k_{-4}/k_1)^{1/2}[k_2/(k_2 + k_{-3})] \approx 1.6. \qquad \text{(IX)}$$

Using the accepted assumption that $k_2 \gg k_3$ and assuming that $2k_t = 8 \cdot 10^8$ L mol^{-1} s^{-1} (average rate constant of disproportionation of semiquinone radicals**[12]**), we obtain the following inequality from the parameter of Eq. (V)

$$k_1{}^{1/2}k_3 \approx 2.8 \cdot 10^3 \text{ L}^{3/2} \text{ mol}^{-3/2} \text{ s}^{-3/2}. \qquad \text{(X)}$$

Multiplication of Eqs (IX) and (X) and insertion of the known**[3]** value $k_{-4} = 6.4 \cdot 10^{-3}$ L mol^{-1} s^{-1} into the result gives

$$k_3/(1 + k_{-3}/k_2) \approx 5.5 \cdot 10^4 \text{ L mol}^{-1} \text{ s}^{-1}. \qquad \text{(XI)}$$

The absolute k_3 value can be estimated from relation (XI), if the ratio of the reaction rate constants k_{-2} and k_{-3} is determined from the heat effects of reactions (−2) and (−3). In reaction (−2) dichloroquinone **4** is reduced to radical $\mathbf{6}^{\bullet}$ in which the strength of the forming O—H bond is D_{OH} = 253.6 kJ mol^{-1}.**[9]** Simultaneously this reaction involves the cleavage of either the O—H bond in 4-hydroxydiphenylaminyl radical $\mathbf{7}_{\mathbf{N}}{}^{\bullet}$ (D_{OH} = 259.5 kJ mol^{-1})**[11]** or the N—H bond in isomeric 4-anilinophenoxy radical $\mathbf{7}_{\mathbf{O}}{}^{\bullet}$ (D_{NH} = 273.6 kJ mol^{-1}).**[11]** In any case, reaction (−2) is endothermic. In reaction (−3) radical $\mathbf{6}^{\bullet}$ is reduced to hydroquinone **3** in which the strength of the forming O—H bond is D_{OH} = 362.4 kJ mol^{-1}.**[9]** The O—H bond (D_{OH} = 339.3 kJ mol^{-1})**[11]** or the N—H bond (D_{NH} = 353.4 kJ mol^{-1})**[11]** in 4-hydroxydiphenylamine **2** is simultaneously broken. It is seen that reaction (−3) is exothermic anyway. The reactions of H atom abstraction by quinones and phenoxy radicals in the intersecting parabolas method are attributed to the same class of elementary reactions and, therefore, the rate constants of reactions (−2) and (−3) are determined from their heat effects only.**[13]** It follows from this that $k_{-3} > k_{-2}$. As mentioned above, $k_2 > k_3$. Since the equilibrium constant K of the reaction of compounds **1** and **3** equals to the product $K = K_2K_3 = (k_2/k_{-2})(k_3/k_{-3})$**[6]** and is close to unity (K = 0.31)**[9]** (see Fig. 1), we conclude that $k_2 \approx k_{-3}$ and $k_{-2} \approx k_3$. Then using expression (XI) we can estimate

$$k_3 \approx 1.1 \cdot 10^5 \text{ L mol}^{-1} \text{ s}^{-1}, \qquad \text{(XII)}$$

and using formula (X)

$$k_1 \approx 6.5 \cdot 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}. \qquad \text{(XIII)}$$

Finally, dividing the parameter in Eq. (VII) into the parameter of Eq. (V) and assuming that $k_2 \gg k_3 \approx k_{-2}$, we get

$$[(k_1 + k_{-6})/k_1]^{1/2} = 0.8,$$

from where

$$k_{-6} \approx 0.27k_1 \approx 1.7 \cdot 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}. \qquad \text{(XIV)}$$

Calculation of the reaction rate constants k_1, k_2, and k_3 from the dependence of the initial reaction rate on the concentration of the starting substances. We processed the experimental data presented in Figs 4 and 5 using formula (IV) and taking into account the above presented estimates (V)—(XIV). The following procedure was used. We specified (held stationary) $k_1 = 1 \cdot 10^{-4}$ L mol^{-1} s^{-1}

and using the iteration method determined the k_2 and k_3 values for which formula (IV) describes most precisely each experimental curve (see Figs 4 and 5). After this we specified $k_1 = 2 \cdot 10^{-4}$ L mol^{-1} s^{-1} and determined a new set of k_2 and k_3. The procedure was repeated with the increment $k_1 = 1 \cdot 10^{-4}$ in the interval $k_1 = (1—15) \cdot 10^{-4}$ L mol^{-1} s^{-1}. Then we compared all obtained sets of k_1, k_2, and k_3 and found that the best agreement of the results (and satisfactory agreement with estimates (V)—(XIV)) is observed at the k_1 values lying in the interval $(2—5) \cdot 10^{-4}$ L mol^{-1} s^{-1}. This k_1 range was additionally studied with the increment $k_1 = 5 \cdot 10^{-5}$ L mol^{-1} s^{-1}. As a result, $k_1 = (3.5\pm1) \cdot 10^{-4}$ L mol^{-1} s^{-1} was found as the best value. The k_2 and k_3 values obtained for each series of runs at $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1} are shown in Figs 4 and 5.

As a whole, when studying the dependences of the initial reaction rate, we obtained the following results (k, L mol^{-1} s^{-1}): $k_1 = (3.5\pm1) \cdot 10^{-4}$, $k_2 = (2.1\pm0.7) \cdot 10^6$, and $k_3 = (2.9\pm0.6) \cdot 10^5$.

Effect of the final products on the initial reaction rate. *Dependence of the initial reaction rate on the 4-hydroxydiphenylamine (2) concentration.* The experiments show that in the presence of final product **2** the initial reaction rate w_1 increases, although the equilibrium shifts toward the initial substances. These data indicate unambiguously that the mechanism of the reaction is complicated, because if the forward reaction of compounds **1** and **3** and the backward reaction of compounds **4** and **2** were one-step, then additives of the final products would induce only a decrease in w_1.

As can be seen from the data in Fig. 7, the curves of the plot of w_1 *vs.* $[\mathbf{2}]_0$ have a maximum, whose position depends on the ratio of concentrations of compounds **1** and **3**. Similar dependences have been observed earlier when the effect of additive **2** on the reaction rate of quinoneimine **1** with 2,5-di-*tert*-butylhydroquinone was studied (however, this reaction, unlike that of compounds **1** and **3**, is virtually irreversible, $K_{298\text{K}} \gg 1$).[3,4] The dual accelerating and inhibiting effect of compound **2** is explained by its participation in elementary steps that exert an opposite effect on the rate of the overall reaction. In the presence of additive **2** in the system, additional initial reaction (–4) occurs from the very beginning, which accelerates the interaction of compounds **1** and **3**. Along with this, the rate of backward reaction (–3) increases more and more strongly with an increase in the concentration of compound **2**, due to which the chain length of the forward chain reaction shortens to decrease its rate.

From Eq. (II) we obtain the formula for the reaction rate in the presence of additive **2**

$$w_1 = \frac{k_2k_3[\mathbf{1}]^{3/2}[\mathbf{3}]}{k_t^{1/2}(k_2[\mathbf{1}]+k_3[\mathbf{3}]+k_{-3}[\mathbf{2}])}\sqrt{k_1[\mathbf{3}]+k_{-4}[\mathbf{2}]}. \qquad \text{(XV)}$$

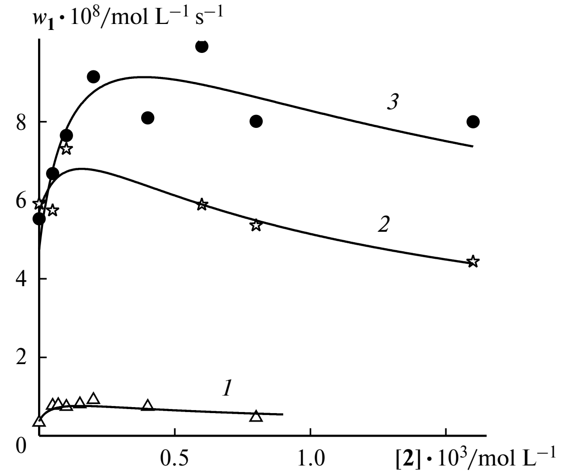

Fig. 7. Plots of the initial rate of the reaction of compounds **1** and **3** *vs.* concentration of product **2**. Initial concentrations of compounds **1** and **3** ($\cdot 10^4$, mol L^{-1}): 2.0 and 2.0 (*1*); 2.0 and 12.0 (*2*); 6.0 and 6.0 (*3*), respectively. Points are experiment, and lines are calculation by formula (XV) at $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1}, $k_{-4} = 6.4 \cdot 10^{-3}$ L mol^{-1} s^{-1} and the following $k_2 \cdot 10^{-6}$, $k_3 \cdot 10^{-5}$, and $k_{-3} \cdot 10^{-6}$ values, L mol^{-1} s^{-1}: 1.65, 1.70, and 2.30 (*1*); 2.72, 2.13, and 2.78 (*2*); 1.00, 2.51, and 1.80 (*3*), respectively. Chlorobenzene, 298.2 K, Ar bubbling.

The k_{-4} value in chlorobenzene at 298 K was determined[3]: $k_{-4} = 6.4 \cdot 10^{-3}$ L mol^{-1} s^{-1}. The reliable estimates for k_1, k_2, and k_3 were presented above. Thus, the data in Fig. 7 can be used to determine k_{-3}.

We also used another, more general approach: the experimental data (see Fig. 7) were processed by formula (XV) using the iteration methods according to the procedure similar to that described above. Each curve in Fig. 7 was processed at fixed k_1 values in the interval $(2—5) \cdot 10^{-4}$ L mol^{-1} s^{-1} with an increment of $5 \cdot 10^{-5}$ L mol^{-1} s^{-1}, and every time we obtained a set of the rate constant values k_2, k_3, and k_{-3}. The value $k_{-4} = 6.4 \cdot 10^{-3}$ L mol^{-1} s^{-1} was not varied. A comparison of thus obtained data showed that the best agreement of the results is achieved again at $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1}. The sets of the k_2, k_3, and k_{-3} values determined at this k_1 value are presented in Fig. 7.

Thus, the study of the dependence of w_1 on the concentration of compound **2** provided the following results (k, L mol^{-1} s^{-1}): $k_1 = 3.5 \cdot 10^{-4}$, $k_2 = (1.8\pm0.5) \cdot 10^6$, $k_3 = (2.1\pm0.3) \cdot 10^5$, and $k_{-3} = (2.3\pm0.3) \cdot 10^6$.

Dependence of the initial reaction rate on the concentration of 2,5-dichloroquinone. As can be seen from the data in Fig. 8, additives of dichloroquinone **4** exert only a weak inhibition effect on the reaction of compounds **1** and **3**. We have earlier observed a similar effect of 2,5-dimethylquinone additives on the chain reaction of quinonenimine **1** with 2,5-dimethylhydroquinone (it is virtually irreversible[14]). From Eq. (2) we obtain the for-

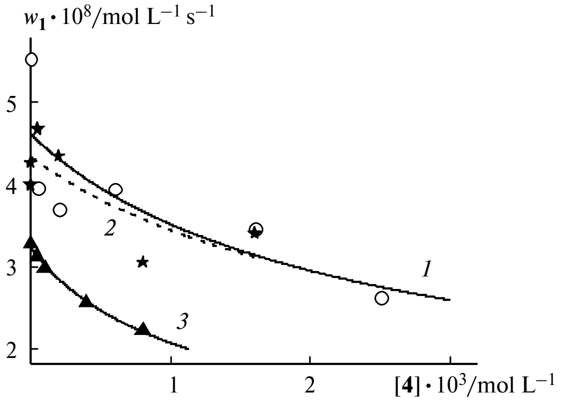

Fig. 8. Plots of the initial rate of the reaction of compounds **1** and **3** *vs.* concentration of product **4**. Initial concentrations of compounds **1** and **3** ($\cdot 10^4$, mol L^{-1}): 6.0 and 6.0 (*1*); 2.0 and 12.0 (*2*); 4.0 and 6.0 (*3*), respectively. Points are experiment, and lines are iteration calculation by formula (XVI) at $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1} and the following $k_2 \cdot 10^{-6}$, $k_3 \cdot 10^{-5}$, $k_{-2} \cdot 10^{-5}$, and $k_{-6} \cdot 10^4$ values, L mol^{-1} s^{-1}: 1.95, 2.15, 9.37, and 1.51 (*1*); 1.43, 2.09, 3.15, and 0.41 (*2*); 1.31, 2.05, 5.03, and 0.44 (*3*), respectively. Chlorobenzene, 298.2 K.

mula for the reaction rate in the presence of dichloroquinone **4**

$$w_1 = \frac{k_2 k_3 [\mathbf{1}][\mathbf{3}]^{3/2}}{k_t^{1/2}(k_2[\mathbf{1}] + k_3[\mathbf{3}] + k_{-2}[\mathbf{4}])}\sqrt{k_1[\mathbf{1}] + k_{-6}[\mathbf{4}]}. \qquad \text{(XVI)}$$

Formula (XVI) is analogous to formula (XV) for the dependence of w_1 on the concentration of compound **2** and, therefore, the different shapes of the curves in Figs 7 and 8 indicate that at close concentrations of compounds **2** and **4** the value $k_{-4}[\mathbf{2}] \gg k_{-6}[\mathbf{4}]$ or that $k_{-4} \gg k_{-6}$. The data in Fig. 8 were used to estimate the k_{-2} and k_{-6} values by the iteration method. In this case, k_1 had the fixed value $k_1 = 3.5 \cdot 10^{-4}$ L mol^{-1} s^{-1}, and k_2 and k_3 were varied in the ranges $(1.3—2.8) \cdot 10^6$ and $(1.8—3.5) \cdot 10^5$ L mol^{-1} s^{-1}, respectively. Thus determined reaction rate constant values are shown in Fig. 8. As a whole, in the study of the dependence of w_1 on the concentration of dichloroquinone **4** we obtained the following results (k, L mol^{-1} s^{-1}): $k_2 = (1.6 \pm 0.3) \cdot 10^6$, $k_3 = (2.1 \pm 0.1) \cdot 10^5$, $k_{-2} = (6 \pm 2.5) \cdot 10^5$, and $k_{-6} = (0.8 \pm 0.4) \cdot 10^{-4}$.

As can be seen, the rate constants of elementary steps of the chain reaction determined by us using different methods in the present work agree satisfactorily with each other. The averaged rate constants of the elementary steps (see Scheme 2) are given below (chlorobenzene, $T = 298.2$ K).

Parameter	k/L mol^{-1} s^{-1}	Parameter	k/L mol^{-1} s^{-1}
k_1	$(3.5 \pm 1) \cdot 10^{-4}$	$2k_{-1}$	$8 \cdot 10^8$
k_2	$(1.8 \pm 0.7) \cdot 10^6$	k_{-2}	$(6 \pm 2.5) \cdot 10^5$
k_3	$(2.4 \pm 0.6) \cdot 10^5$	k_{-3}	$(2.3 \pm 0.3) \cdot 10^6$
$2k_4$	$8 \cdot 10^8$	k_{-4}	$6.4 \cdot 10^{-3}$ [3]
$2k_5$	$8 \cdot 10^8$	k_{-5}	?
$2k_6$	$8 \cdot 10^8$	k_{-6}	$(0.8 \pm 0.4) \cdot 10^{-4}$

Thus, the rate constants of almost all elementary steps of the chain reaction of compounds **1** and **3**, which has a pronounced reversible character, were reliably estimated for the first time from the experimental data. We confirmed thus the earlier proposed mechanism of interaction in quinoneimine—hydroquinone systems and showed that the relations obtained by the kinetic analysis are valid.

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