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CHEMICAL KINETICS AND CATALYSIS

Kinetics and Mechanism of the Chain Reaction of *N*,*N*'-Diphenyl-1,4-benzoquinone Diimine with Thiophenol in Chlorobenzene

V. T. Varlamov and A. V. Gadomska

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

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Abstract—The regularities of the reaction of *N*,*N*'-diphenyl-1,4-benzoquinone diimine with thiophenol in chlorobenzene at 343 K were studied by kinetic spectrophotometry. The reaction orders were determined for the components under the conditions when the concentration of thiophenol considerably exceeded that of quinone diimine: $n_{\mathrm{QDI}} = 1.5$ for quinone diimine and $n_{\mathrm{PhSH}} = 1.0$ for thiophenol. The initiators (azo-*bis*-isobutyronitrile and tetraphenylhydrazine) were found to considerably accelerate the reaction, which suggests that the reaction proceeded by the chain mechanism. The reaction chain length changed from one dozen to several dozens of units depending on the experimental conditions. The chain mechanism (kinetic scheme) of the reaction was suggested; it agrees with the experimental data, according to which the chains are initiated simultaneously by the second and third order reactions between quinone diimine and thiophenol. The rate constants of these stages at 343 K were determined: $k_{\mathrm{bi}} = 0.014 \pm 0.002$ L mol^{-1} s^{-1}; $k_{\mathrm{tri}} = 22.8 \pm 1.8$ L^2 mol^{-2} s^{-1}. The limiting stage of chain propagation was concluded to be the reaction of the thiyl radical with quinone diimine; the rate constant of this stage was evaluated: $k_{\mathrm{pr}} \sim 1.3 \times 10^6$ L mol^{-1} s^{-1} at 343 K.

Keywords: *N*,*N*'-diphenyl-1,4-benzoquinone diimine, thiophenol, radical reaction, kinetics, initiator effect, chain mechanism, elementary stages, rate constants.

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INTRODUCTION

Quinone compounds (quinones and their nitrogen analogs quinone imines) are highly reactive compounds involved in many chemical processes. An analysis of the literature data shows that the majority of studies were mainly devoted to heterolytic reactions [1–4], while the radical reactions have been studied insufficiently [5]. However, several known reactions of quinone compounds occur by the free radical mechanism, but not by heterolysis, as believed earlier. For example, the reversible reactions of quinone imines with hydroquinones in chlorobenzene proceed by the radical-chain but not ionic mechanism [6, 7], and the chain length of these reactions can be very long, up to a few hundred thousand units [8].

Recently, the homolytic mechanism was found for another class of reactions involving quinone compounds. The reaction of *N*,*N*'-diphenyl-1,4-benzoquinone diimine (C_6H_5–N=C_6H_4=N–C_6H_5, QDI) with 2-mercaptobenzothiazole in chlorobenzene was studied and it was shown on this example that the reactions of quinone compounds with thiols also occur by the radical-chain mechanism [9], though earlier they were considered to occur by the nucleophilic 1,4-addition of thiol to the cyclohexadiene ring of quinone or quinone imine [1–3, 10, 11]. The mechanism of these reactions adopted earlier was based on the results of the analysis of the composition of the reaction products (mainly in polar media) and on the fact of considerable increase in the reaction rate at increased solvent polarity, but there were no detailed kinetic studies of the mechanism. Note that a detailed mechanism of the radical reactions of quinone imines with thiols for the reaction of QDI with 2-mercaptobenzothiazole has not yet been found because of serious difficulties related to the thiol–thione isomerism of 2-mercaptobenzothiazole. Therefore, we sought simpler quinone imine–thiol systems and found that the reactions of QDI with thiophenol (C_6H_5SH, PhSH) and *n*-decylthiol also occurred by the radical chain mechanism; some preliminary data on these reactions were given in [12].

The reactions of quinone compounds with thiols are very important in chemistry and biochemistry. They occur during the ageing of rubber in air [13–15] and in biological systems and are one of the main reasons for high toxicity of quinone compounds that enter the organism from the environment and as drugs and/or their metabolites [16–18]. Their toxicity is explained by the fact that quinone compounds bind irreversibly S–H group of the sulfur-containing compounds such as the cysteine moieties of the protein molecules. In view of the great importance of the reactions of quinone compounds with thiols in both nonpolar and polar media, here we studied in detail the kinetics of the reaction of QDI with PhSH in the relatively low-polar aromatic solvent chlorobenzene.

EXPERIMENTAL

The kinetics of the reaction of QDI with PhSH was studied by kinetic spectrophotometry. The experiments were performed at $T = 343 \pm 0.2$ K under argon in bubble-type quartz cell reactors (volume 6.5 or 8.5 mL, thickness $l = 2.0$ cm) built in Specord UV VIS and Specord M 40 spectrophotometers. The reaction was monitored according to the consumption of QDI, recording (at intervals of no more than 1 s) the optical density of the solution (displaying it on computer) in the absorption region of QDI at 22260 ($\varepsilon = 6730$), 20000 ($\varepsilon = 3755$), or 19000 cm^{-1} ($\varepsilon = 1690$ L mol^{-1} cm^{-1} [19]) at different initial concentrations of QDI. Before the work in the monitoring mode, preliminary experiments were performed, while intermittently recording the spectra over the whole visible range accessible for measurements. Such experiments were necessary in order to clarify whether QDI is the only substance that absorbs at the analytical wavelength in the course of the reaction.

The procedures for the synthesis and purification of QDI and the tetraphenylhydrazine $(C_6H_5)_2N-N(C_6H_5)_2$ (TPH) initiator were described in [20]. Thiophenol PhSH (Aldrich, ⩾99%) was used without further purification. As a solvent, we used chlorobenzene (Aldrich) thoroughly purified by the procedure of [20]. Azo-*bis*-isobutyronitrile (AIBN) (Fluka) was purified by the procedure of [12] by passing a saturated benzene solution of AIBN through a silica gel column, evaporating the eluate at room temperature, separating the crystals, washing them on a filter, drying them in vacuum, and recrystallizing from methanol.

For the TPH and AIBN initiators, we used the following initiation rate constants at 343 K: $k_i(\text{TPH}) = 1.96 \times 10^{-4}$ s^{-1} [7] and $k_i(\text{AIBN}) = 4.51 \times 10^{-5}$ s^{-1} [21].

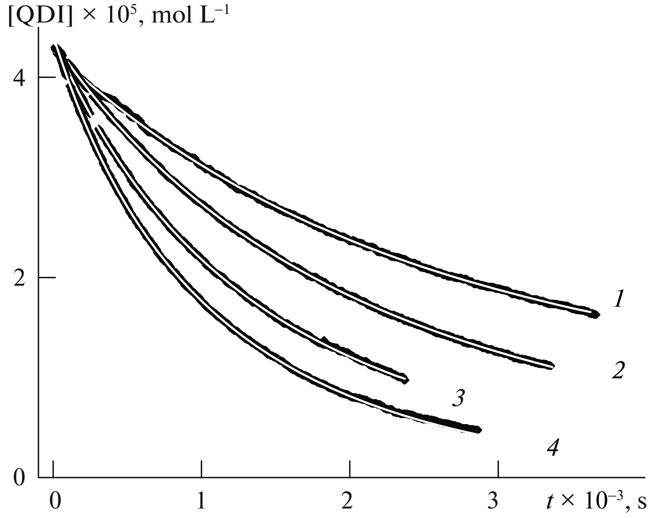


Fig. 1. Accelerating action of the tetraphenylhydrazine initiator on the reaction of QDI with PhSH. The reagent concentrations in the experiments were constant: $[\text{QDI}]_0 = 4.3 \times 10^{-5}$, $[\text{PhSH}]_0 = 6.88 \times 10^{-4}$ mol L^{-1}; the initiation rates $w_{i(I)} \times 10^9$, mol L^{-1} s^{-1}: (*1*) 0 (without initiator), (*2*) 1.52, (*3*) 3.80, and (*4*) 7.60. Merged black dots: experimental data; white lines: approximation of the kinetic curves by function (1). Chlorobenzene, 343 K, Ar bubbling.

RESULTS AND DISCUSSION

Most of the experiments were performed under the conditions when the concentration of PhSH was significantly higher than that of QDI, which facilitated the interpretation of the results. The kinetic regularities were studied from the initial QDI consumption rates (w_{QDI}). To determine w_{QDI}, we used the approximation of the experimental QDI consumption curves by any suitable analytical function when the initial reaction rate was calculated from the derivative of this function at $t = 0$. The approximation technique considerably increases the accuracy of w_{QDI} compared with the accuracy obtained when seeking w_{QDI} from the envelope of the curve at $t = 0$, especially if the number of experimental points amounts to hundreds and thousands. The curves were well approximated by the function

$$[\text{QDI}] = a_1 e^{-b_1 t} + a_2 e^{-b_2 t}, \tag{1}$$

where a_1, a_2, b_1, and b_2 are the constants (parameters), whose numerical values were chosen by iterations. Function (1) approximated the QDI consumption curves to high accuracy and large depths even in cases when the concentrations of the QDI and PhSH reagents were comparable (Fig. 1). In accordance with (1), w_{QDI} was calculated by the equation

$$w_{\text{QDI}} = -d[\text{QDI}]/dt = a_1 b_1 + a_2 b_2. \tag{2}$$

Reaction orders with respect to the components. To determine the reaction orders, we constructed the dependences of w_{QDI} on the reagent concentrations in series of experiments at constant concentration of one component and variable concentration of the other. The dependences of w_{QDI} on $[\text{QDI}]_0$ at $[\text{PhSH}]_0$ = const were nonlinear and nicely approximated by the power function

$$w_{\text{QDI}} = f[\text{QDI}]_0^{n_{\text{QDI}}},$$

where f is the coefficient. For experiments at $[\text{PhSH}]_0$ = const = 1.38×10^{-3} and 2.06×10^{-3} mol L^{-1} and varying $[\text{QDI}]_0$ from 0 to 1.3×10^{-4} mol L^{-1}, iterations gave $n_{\text{QDI}} = 1.48 \pm 0.17$ and 1.40 ± 0.11, respectively, for series 1 and 2. That is, the reaction order with respect to QDI is 1.5 within the accuracy of experiments. The

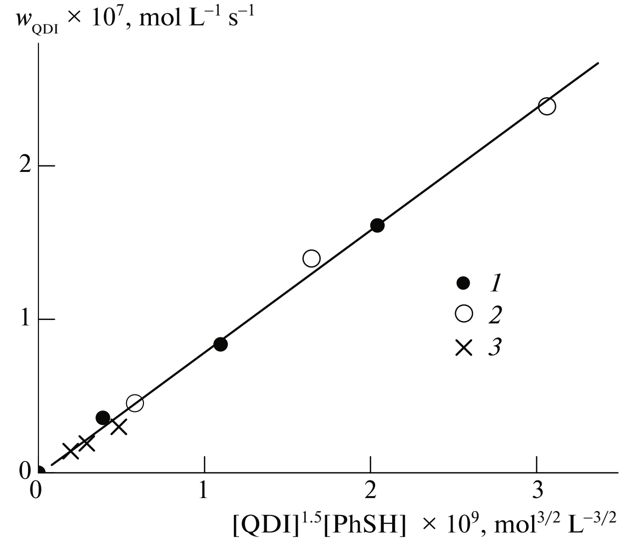


Fig. 2. Dependence of the initial reaction rate on the parameter $[QDI]_0^{3/2}[PhSH]_0$: (*1*) series 1, (*2*) series 2 (see text), and (*3*) series of experiments at $[QDI]_0 = 4.3 \times 10^{-5}$ and $[PhSH]_0 = 6.88 \times 10^{-4}$, 1.03×10^{-3}, and 1.72×10^{-3} mol L^{-1}. Chlorobenzene, 343 K, Ar bubbling.

results of similar experiments on the dependencies of w_{QDI} at constant QDI concentration and variable PhSH concentration indicated that $n_{PhSH} = 1.0$.

It followed from the obtained data that for the reaction rate,

$$w_{QDI} = g[PhSH][QDI]^{3/2}, \tag{3}$$

where *g* is the coefficient. Figure 2 presents the results of the processing of the experimental data in coordinates of (3). It can be seen that the relationship between w_{QDI} and the $[PhSH][QDI]^{3/2}$ parameter is really linear and passes through the origin of coordinates (the cut on the ordinate axis is $(1.3 \pm 2.9) \times 10^{-9}$ mol L^{-1} s^{-1}, i.e., zero within the accuracy of experiment), and the slope is $g = 79.6 \pm 2.0$ L$^{3/2}$ mol$^{3/2}$ s^{-1}. Thus,

$$w_{QDI} = (79.6 \pm 2.0)[PhSH][QDI]^{3/2}. \tag{3a}$$

Earlier, we reported that $n_{QDI} = 1.0$ [12]. Here, the reaction order was studied more thoroughly, and the value found earlier $n_{QDI} = 1.0$ is believed to be inaccurate.

Kinetics of the initiated reaction. The fractional order for QDI suggested a complex reaction mechanism. It was not excluded that the reaction occurs by the chain mechanism. To verify this assumption, we performed experiments in the presence of initiators (I), namely, AIBN and tetraphenylhydrazine. It was found that the initiator accelerates the reaction, but the nature of the initiator was insignificant. Therefore, in the majority of experiments, we used tetraphenylhydrazine, which is more convenient to handle. The initiator considerably accelerated the reaction (Fig. 1), which suggested its chain mechanism. Function (1) also described the QDI consumption curves with high accuracy in experiments with the initiator, and therefore it has been used by us in this case too.

The majority of liquid-phase chain reactions have quadratic-law chain termination mechanism and at moderate and long chains, their rate is described by the equation [22]

$$w_{QDI} = A w_{i\Sigma}^{1/2}, \tag{4}$$

where *A* is the parameter whose form is determined by the nature of the chain propagation and termination stages, and $w_{i\Sigma}$ is the total rate of radical generation equal to the sum of the chain generation due to own processes in the system w_{i0} and the radical generation rate $w_{i(I)}$ due to the decomposition of the initiator I: $w_{i(I)} = k_i[I]$.

Since

$$w_{i\Sigma} = w_{i0} + w_{i(I)},$$

Eq. (4) can be transformed into

$$w_{QDI} = A w_{i\Sigma}^{1/2} = A(w_{i0} + w_{i(I)})^{1/2}. \tag{4a}$$

If the chain termination occurs by reaction between two radicals of the same sort, the *A* parameter in (4) and (4a) is calculated by the equation

$$A = \frac{k_{pr}}{(k_t)^{1/2}}[Sub], \tag{5}$$

where k_{pr} is the rate constant of the limiting stage of chain propagation involving one of the chain-carrier radicals and one of the starting substances temporarily denoted as Sub (QDI or PhSH), and k_t is the rate constant of chain termination on the chain-carrier radicals.

Equation (4a) can be recorded as

$$w_{QDI}^2 = A^2 w_{i0} + A^2 w_{i(I)}. \tag{6}$$

At relatively high w_{i0} values, this form of the dependence of w_{QDI} on $w_{i(I)}$ is more convenient for data treatment than (4a). According to (6), the square of the reaction rate w_{QDI}^2 should increase linearly with the initiation rate $w_{i(I)}$. The A^2 (and hence *A*, see (5)) parameter can be determined from the slope of this dependence; then the nature of the substrate Sub can be determined and the parameter $k_{pr}/\left(k_t^{1/2}\right)$ can be calculated from the dependence of *A* on the nature of the reagent.

Figure 3 presents the dependences of w_{QDI}^2 on $w_{i(I)}$ in experiments at a constant QDI concentration but at PhSH concentrations that differ from series to series. All the lines in Fig. 3 are parallel to one another within the accuracy of experiment; i.e., A^2 (and hence *A*) is independent of [PhSH]. Using the slopes in Fig. 3, we

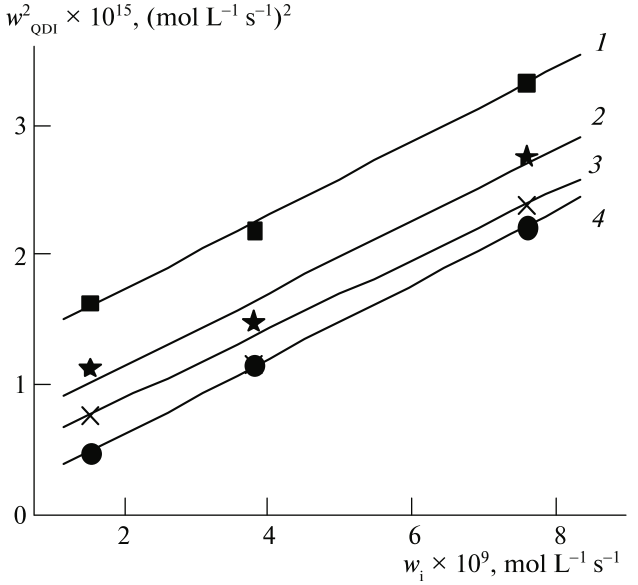


Fig. 3. Dependences of w^2_{QDI} on $w_{i(I)}$ at constant (in series) concentrations of [PhSH] × 10^3, mol L^{-1}: (*1*) 2.75, (*2*) 1.72, (*3*) 1.03, and (*4*) 0.688. In all experiments, $[QDI]_0$ = const = 4.3 × 10^{-5} mol L^{-1}. Tetraphenylhydrazine initiator.

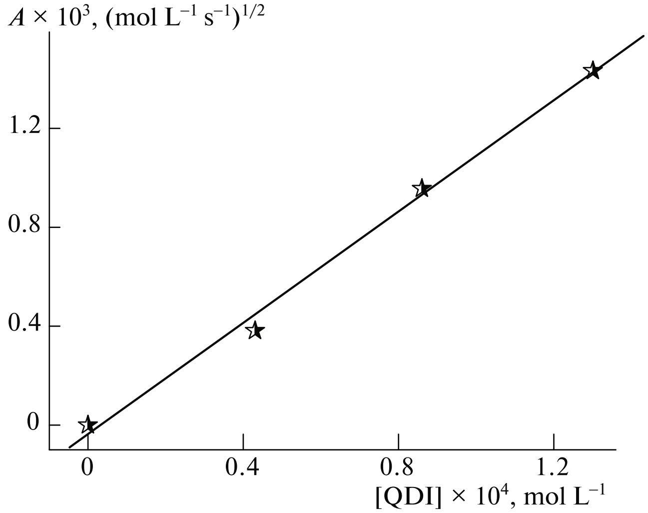


Fig. 4. Dependence of the A parameter on the QDI concentration constructed based on the linear dependences of w^2_{QDI} on $w_{i(I)}$ in three series of experiments at $[PhSH]_0$ = const = 6.88 × 10^{-4} mol L^{-1}. Tetraphenylhydrazine initiator.

found the A^2 value averaged over four series of experiments at $[QDI]_0$ = const = 4.3 × 10^{-5} mol L^{-1}: A^2 = (2.78 ± 0.09) × 10^{-7} mol L^{-1} s^{-1}, from which

$$A = (5.27 \pm 0.09) \times 10^{-4}\ (\text{mol L}^{-1}\ \text{s}^{-1})^{1/2}. \qquad (7)$$

We also constructed similar dependences of w^2_{QDI} on $w_{i(I)}$ for series of experiments at a constant concentration of $[PhSH]_0$ = 6.88 × 10^{-4} mol L^{-1} and different concentrations of QDI that were constant in series. These dependences were also linear, but the slopes of the lines depended on the QDI concentration. The *A* parameter was calculated for three series of experiments and the dependence of *A* on the QDI concentration was determined using the data of the above dependences (Fig. 4). It can be seen that there is a linear dependence between *A* and the QDI concentration and the line in Fig. 4 passes through the origin of coordinates:

$$A = \frac{k_{pr}}{(k_t)^{1/2}}[\text{Sub}]$$
$$= -(3.6 \pm 4.7) \times 10^{-5} + (11.3 \pm 0.6)[\text{QDI}]_0.$$

The results indicate that

$$\text{Sub} \equiv \text{QDI}. \qquad (8)$$

In this case, from the data in Fig. 4 we obtain that $k_{pr}/k_t^{1/2} = 11.3 \pm 0.6$ (L mol^{-1} s^{-1})$^{1/2}$.

The independent $k_{pr}/(k_t)^{1/2}$ value can be determined from the data in Fig. 3. Since the experiments corresponding to the data of Fig. 3 were performed under the conditions $[QDI]_0$ = const = 4.3 × 10^{-5} mol L^{-1}, we obtain, based on (7), that

$$k_{pr}/(k_t)^{1/2} = A/[\text{QDI}]_0$$
$$= (5.27 \pm 0.09) \times 10^{-4}/4.3 \times 10^{-5}$$
$$= 12.3 \pm 0.2\ (\text{L mol}^{-1}\ \text{s}^{-1})^{1/2},$$

which only slightly differs from the above-given value.

Reaction mechanism. To describe and interpret the experimental kinetic data, we suggested a mechanism of the reaction of QDI with PhSH presented as a kinetic scheme below (the simplified variant was suggested earlier [12]):

$$\text{I} \longrightarrow \text{Ph}_2\text{N}^\bullet \xrightarrow{+\text{PhSH}} \text{PhS}^\bullet, \qquad (i)$$

$$\text{QDI} + \text{PhSH} \xrightarrow{k_{1bi}} \text{HQDI}^\bullet + \text{PhS}^\bullet, \qquad (\text{I})$$

$$\text{PhSH} + \text{QDI} + \text{PhSH}$$
$$\xrightarrow{k_{1tri}} \text{PhS}^\bullet + \text{H}_2\text{QDI} + \text{PhS}^\bullet, \qquad (\text{I}')$$

$$\text{HQDI}^\bullet + \text{PhSH} \longrightarrow \text{H}_2\text{QDI} + \text{PhS}^\bullet,$$

$$\text{PhS}^\bullet + \text{QDI} \xrightarrow{k_2} \text{AmN}^\bullet\text{Ph}, \qquad (\text{II})$$

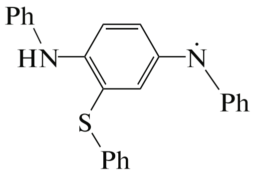
$$\text{AmN}^\bullet\text{Ph} + \text{PhSH} \xrightarrow{k_3} \text{AmNHPh} + \text{PhS}^\bullet, \qquad (\text{III})$$

$$\text{PhS}^\bullet + \text{PhS}^\bullet \xrightarrow{k_4} \text{PhSSPh}, \qquad (\text{IV})$$

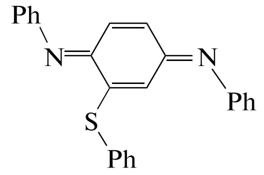
$$\mathrm{PhS}^\bullet + \mathrm{AmN}^\bullet\mathrm{Ph} \xrightarrow{k_5} \mathrm{PhSH} + \mathrm{PhS\text{-}QDI}, \quad \text{(V)}$$

where

$\mathrm{AmN}^\cdot\mathrm{Ph} =$

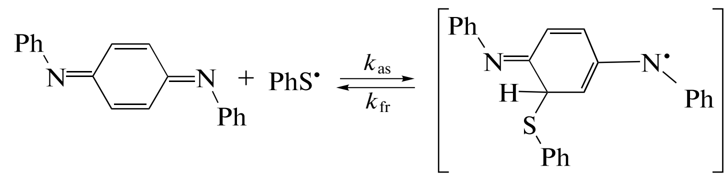


$\mathrm{PhS{-}QDI} =$



According to this mechanism, the phenylthiyl $C_6H_5S^\cdot$ ($PhS^\cdot$) and 4-anilinediphenylamyl $C_6H_5{-}N^\cdot{-}C_6H_4{-}NH{-}C_6H_5$ ($HQDI^\cdot$) radicals form in the absence of an initiator by the direct second and third order reactions (I) and (I') of QDI with PhSH. The third order reaction possibly involves the stage of the formation of the intermediate QDI...PhSH complex, which then reacts with another PhSH molecule, though true trimolecular reactions were reported with radical generation from three molecules and one-stage cleavage of two old bonds and formation of two new ones [23]. The $HQDI^\cdot$ radicals are quickly replaced by $PhS^\cdot$ radicals by radical exchange with PhSH, so that each of the stages (I) and (I') can be regarded as the generation of two $PhS^\cdot$ radicals in a kinetic description. The $PhS^\cdot$ radicals are considered to be chain-carrier radicals in the overall reaction of PhSH with QDI. Chain propagation (II) involving the $PhS^\cdot$ radicals is actually complex. It includes the stage of $PhS^\cdot$ association with the cyclohexadiene fragment of QDI in the radical adduct $RA^\cdot$ with the rate constant k_{as} and defragmentation of the $RA^\cdot$ adduct into the starting reagents $PhS^\cdot$ and QDI with the rate constant k_{fr}, as well as isomerization of $RA^\cdot$ into the diarylaminyl radical $AmN^\cdot Ph$ with the rate constant k_{iso}:

$$\mathrm{RA}^\bullet \xrightarrow{k_{iso}} \mathrm{AmN}^\bullet\mathrm{Ph}.$$



(RA•)

Several authors reported the reversible formation of the radical adduct by the reaction of thiyl radicals with unsaturated carbon–carbon bonds of olefins [24–26]. In the suggested mechanism, this reaction complemented with possible isomerization of $RA^\cdot$ into $AmN^\cdot Ph$ is regarded as one of the stages of chain propagation in the chain reactions of thiols with quinone compounds.

In the steady state approximation for $[RA^\cdot]$,

$$k_{as}[\mathrm{QDI}][\mathrm{PhS}^\cdot] = (k_{fr} + k_{iso})[\mathrm{RA}^\cdot]. \quad (9)$$

If $k_{iso} \gg k_{fr}$, the rate of stage (II) can be expressed in the following way:

$$\begin{aligned} w_2 &= k_2[\mathrm{QDI}][\mathrm{PhS}^\bullet] = w_{\mathrm{AmNPh}} \\ &= k_{iso}[\mathrm{RA}^\bullet] = k_{as}[\mathrm{QDI}][\mathrm{PhS}^\bullet] \end{aligned} \quad (9a)$$

and $k_2 = k_{as}$.

If $k_{fr} \gg k_{iso}$, then $[RA^\cdot] = (k_{as}/k_{fr})\,[QDI][PhS^\cdot]$, from which

$$\begin{aligned} w_2 &= k_2[\mathrm{QDI}][\mathrm{PhS}^\bullet] = w_{\mathrm{AmNPh}} = k_{iso}[\mathrm{RA}^\bullet] \\ &= k_{iso}k_{as}/k_{fr}[\mathrm{QDI}][\mathrm{PhS}^\bullet] \end{aligned} \quad (9b)$$

and

$$k_2 = k_{iso}k_{as}/k_{fr}.$$

Stages (IV) and (V) are considered to be chain termination reactions in the suggested mechanism.

If chains are long, from the given scheme we obtain

$$w_{\mathrm{QDI}} = k_2[\mathrm{PhS}^\cdot][\mathrm{QDI}] = k_3[\mathrm{PhSH}][\mathrm{AmN}^\cdot\mathrm{Ph}],$$

from which the radical concentration can be expressed in terms of the reaction rate:

$$\begin{aligned} [\mathrm{PhS}^\bullet] &= w_{\mathrm{QDI}}/(k_2[\mathrm{QDI}]), \\ [\mathrm{AmN}^\bullet\mathrm{Ph}] &= w_{\mathrm{QDI}}/(k_3[\mathrm{PhSH}]). \end{aligned} \quad (10)$$

Substituting (10) into the stationary mode equation

$$\begin{aligned} &2k_{1bi}[\mathrm{QDI}][\mathrm{PhSH}] + 2k_{1tri}[\mathrm{QDI}][\mathrm{PhSH}]^2 \\ &+ w_{i(I)} = 2k_4[\mathrm{PhS}^\bullet]^2 + 2k_5[\mathrm{PhS}^\bullet][\mathrm{AmN}^\bullet\mathrm{Ph}], \end{aligned} \quad (11)$$

we obtain an equation that relates w^2_{QDI} with the initiation rate $w_{i(I)}$ due to the decomposition of the initiator

Effect of reagent concentrations and $w_{i(I)}$ on the chain length of the reaction of QDI with PhSH (343 K, chlorobenzene)

[QDI] × 10^5	[PhSH] × 10^4	w_{QDI} × 10^8	$w_{i(I)}$ × 10^{10}	$w_{i(bi)}$ × 10^{10}	$w_{i(tri)}$ × 10^{10}	ν
mol L^{-1}		mol L^{-1} s^{-1}				
8.60	13.8	8.37	0	33.2	74.2	7.8
13.0	13.8	16.1	0	50.2	112.4	9.9
4.30	6.88	1.40	0	8.28	9.28	8.0
4.30	6.88	3.40	38.0	8.28	9.28	6.1
8.60	0.86	1.13	0	2.08	0.29	47.8
8.60	0.86	2.68	7.60	2.08	0.29	26.9

$w_{i(bi)} = 2k_{1bi}[QDI][PhSH]$, $w_{i(tri)} = 2k_{1tri}[QDI][PhSH]^2$, and ν (units) = $w_{QDI}/(w_{i(I)} + w_{i(bi)} + w_{i(tri)}$.

I recorded in the form of (6):

$$w_{QDI}^2 = A^2 w_{i0} + A^2 w_{i(I)}$$

$$= \frac{k_2^2 k_3 [QDI]^2 [PhSH]}{2k_3k_4[PhSH] + 2k_2k_5[QDI]} \tag{12}$$

$$\times \{2k_{1bi}[QDI][PhSH] + 2k_{1tri}[QDI][PhSH]^2\}$$

$$+ \frac{k_2^2 k_3 [QDI]^2 [PhSH]}{2k_3k_4[PhSH] + 2k_2k_5[QDI]} \times w_{i(I)}.$$

Equation (12) agrees with the experimental data, though under certain conditions. It should be admitted that the chains are mainly terminated by reaction (IV) and the role of cross-disproportionation (V) is insignificant. In this case, based on (5) and (12), we have

$$A = \frac{k_{pr}}{k_t^{1/2}}[Sub] = \frac{k_2}{(2k_4)^{1/2}}[QDI],$$

which agrees with the experimental data present in Figs. 3 and 4. The limiting stage of chain propagation in the suggested mechanism is stage (II) of the reaction of $PhS^{\bullet}$ with QDI; i.e., $k_{pr} = k_2$ in (5).

Based on (12), the equation for w_{QDI} in the absence of an initiator has the form:

$$w_{QDI} = A w_{i0}^{1/2}$$

$$= \frac{k_2}{(2k_4)^{1/2}}[QDI] w_{i0}^{1/2} = \frac{k_2}{(2k_4)^{1/2}}[QDI] \tag{13}$$

$$\times \left\{2k_{1bi}[QDI][PhSH] + 2k_{1tri}[QDI][PhSH]^2\right\}^{1/2}.$$

To coincide this equation with the experimental relation (3), the chain initiation under the conditions of experiments on the determination of the reaction order from the components (see above) should be assumed to occur mainly by the third order reaction (I')

$$w_{i0} = 2k_{1tri}[QDI][PhSH]^{3/2}.$$

In this case,

$$w_{QDI} = \frac{k_2}{(2k_4)^{1/2}}[QDI]\left(2k_{1tri}[QDI][PhSH]^2\right)^{1/2}$$

$$= \mathrm{const} \times [QDI]^{3/2}[PhSH]$$

in accordance with (3). The data obtained allow us to evaluate k_{1tri}. Indeed, $k_2/(2k_4)^{1/2} = 11.8 \pm 0.4$ (L mol^{-1} $s^{-1})^{1/2}$ (see above), and const = $\{k_2/(2k_4)^{1/2}\}(2k_{1tri})^{1/2} = g = 79.6 \pm 2.0$ $L^{3/2}$ $mol^{3/2}$ s^{-1} (see (3a)). From these data, we find that

$$k_{1tri} = 22.8 \pm 2.7 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}. \tag{14}$$

Experiments at equal concentrations. Additional data were obtained from experiments at equal concentrations of the reagents $[QDI]_0 = [PhSH]_0 = c$. When interpreting the results, we took into account that the concentrations in these experiments differed considerably from those in the above-described experiments when the concentration of PhSH significantly exceeded that of QDI. It is not excluded that the nature of the generation and chain termination stages can change under these conditions. Therefore, the results of the experiments at equal concentrations were considered with inclusion of all the stages of the reaction mechanism (see the scheme).

It follows from (12) that at $[QDI]_0 = [PhSH]_0 = c$, the equation for the rate of the noninitiated reaction is

$$w_{QDI} = \left(\frac{k_2^2 k_3}{k_3k_4 + k_2k_5} k_{1bi}\right)^{1/2} c^2 \tag{15}$$

for the case when the radicals form by bimolecular reaction (I) and

$$w_{QDI} = \left(\frac{k_2^2 k_3}{k_3k_4 + k_2k_5} k_{1tri}\right)^{1/2} c^{2/5} \tag{15a}$$

for the case when the radicals form by trimolecular reaction (I').

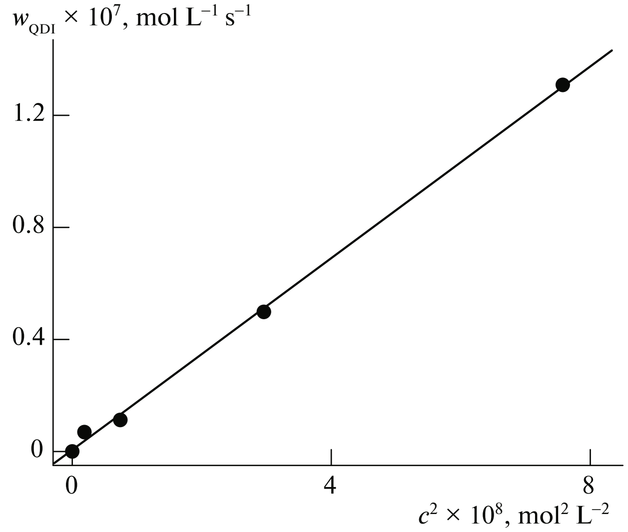


Fig. 5. Dependence of w_{QDI} on the square of equal concentrations of the reagents c_2 (Eq. (15)). Chlorobenzene, 343 K, Ar bubbling.

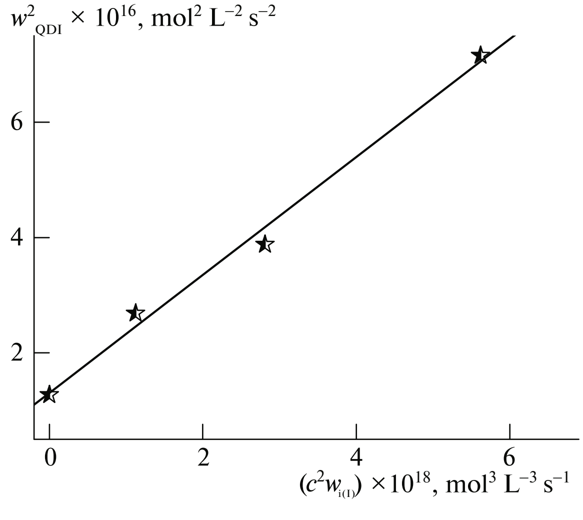


Fig. 6. Treatment of the experimental data in the coordinates $w^2_{QDI} - c^2 w_{i(I)}$ of (17). The reagent concentrations are $[QDI]_0 = [PhSH]_0 = 8.6 \times 10^{-5}$ mol L^{-1}.

Equation (15) is in better agreement with the experimental data than (15a) (Fig. 5). From the slope of the line in Fig. 5 we found value of the parameter:

$$\left(\frac{k_2^2 k_3}{k_3 k_4 + k_2 k_5} k_{1bi}\right)^{1/2} = 1.71 \pm 0.04 \text{ L mol}^{-1} \text{ s}^{-1}. \quad (16)$$

According to (12), at equal reagent concentrations, the results of the experiments in the presence of an initiator should be linearized in the coordinates $w^2_{QDI} - c^2 w_{i(I)}$ of the equation

$$\begin{aligned} w^2_{QDI} &= \frac{(k_{1bi}c^2 + 0.5 w_{i(I)}) k_2^2 k_3 c^2}{k_3 k_4 + k_2 k_5} \\ &= \frac{k_2^2 k_3}{k_3 k_4 + k_2 k_5} k_{1bi} c^4 + 0.5 \frac{k_2^2 k_3}{k_3 k_4 + k_2 k_5} c^2 w_{i(I)}. \end{aligned} \quad (17)$$

According to Fig. 6, (17) is indeed in good agreement with the experimental data:

$$\begin{aligned} &w^2_{QDI}, (\text{mol L}^{-1} \text{ s}^{-1})^2 \\ &= (1.3 \pm 0.2) \times 10^{-16} + (102 \pm 7) c^2 w_{i(I)}. \end{aligned} \quad (18)$$

Taking into account (16) and using the slope of the line (18), we find

$$k_{1bi} = 0.014 \pm 0.002 \text{ mol L}^{-1} \text{ s}^{-1}. \quad (19)$$

Another independent value of k_{1bi} can be obtained by using the parameters of linearization of the results of the experiments with initiator (Fig. 6) in the coordinates $w^2_{QDI} - c^2 w_{i(I)}$ of (18). In these experiments, $c = 8.6 \times 10^{-5}$ mol L^{-1}. We obtained

$$k_{1bi} = 0.012 \pm 0.00 \text{ mol L}^{-1} \text{ s}^{-1}. \quad (19a)$$

Thus, the results indicate that in the experiments with equal concentrations, the chain generation in the noninitiated reaction of QDI with PhSH mainly occurs by the bimolecular reaction. When the concentrations are varied within wide limits, the radicals are generally formed simultaneously by second and third order reactions. The predominance of a definite route depends on the reagent concentration. In the experiments with equal concentrations, the concentrations of the QDI and PhSH reagents are very low (~(0.4–2.5) × 10^{-4} mol L^{-1}); therefore, the radicals are mainly formed by the bimolecular mechanism. At high $[PhSH]_0$ when $k_{1tri}[PhSH]_0 > k_{1bi}$, the third order reaction prevails. According to the data presented above, the dominant mechanism should change at $[PhSH]_0 > k_{1bi}/k_{1tri} = 6 \times 10^{-4}$ mol L^{-1}, which agrees with the experiment (for experimental conditions in determination of the reaction order, see Fig. 2).

Using the obtained values of k_{1tri} and k_{1bi}, we can calculate the chain length for different experimental conditions. These data are presented in the table. According to the table, the chain length is ~10 units in the majority of experiments, but increases considerably in the experiments with equal concentrations. The chain length depends on both the reagent concentration and the radical generation rate due to the decomposition of the initiator $w_{i(I)}$.

Using the obtained data, we can determine the main stage of chain termination in the experiments with equal concentrations. Indeed, according to (17) and (18),

$$\begin{aligned} &\frac{k_2^2 k_3}{k_3 k_4 + k_2 k_5} = k_2^2 \Big/ \left(k_4 + \frac{k_2}{k_3} k_5\right) \\ &= 2 \times (102 \pm 7) = 204 \pm 14 \text{ L mol}^{-1} \text{ s}^{-1}. \end{aligned} \quad (20)$$

According to the data presented above, the averaged value is $k_2/(k_t)^{1/2} = 11.8 \pm 0.4$ (L mol^{-1} s^{-1})$^{1/2}$. We found that under the conditions of the experiments discussed above, chain termination mainly occurs by reaction (IV); i.e., $k_t = 2k_4$ in this case, so that

$$\begin{aligned} k_2^2/k_4 &= 2\times(11.8\pm0.4)^2 \\ &= 280\pm40 \text{ L mol}^{-1}\text{ s}^{-1}. \end{aligned} \tag{20a}$$

The resulting estimates (20) and (20a) are close. This indicates that the denominators in these relations are also close; i.e., $k_4 \gg \frac{k_2}{k_3}k_5$.

This means that in the experiments with equal concentrations, chain termination also occurs mainly by reaction (IV). Finally, the obtained data allow us to evaluate k_2 because the value of k_4 is known: $k_4 = 6 \times 10^9$ L mol^{-1} s^{-1} [27]. From $k_2/(k_t)^{1/2} = k_2/(2k_4)^{1/2} = 11.8$ (L mol^{-1} s^{-1})$^{1/2}$ we obtain $k_2 = 1.3 \times 10^6$ L mol^{-1} s^{-1}. This estimate agrees well with the literature data on the rate constants of the elementary reactions of PhS$^\bullet$ radicals with double carbon–carbon bonds [28–30].

CONCLUSIONS

Thus, we have studied in detail the kinetics of the reaction of quinone diimine QDI with thiophenol PhSH in chlorobenzene. Based on the obtained data, a kinetically substantiated radical chain mechanism was suggested for the reaction in the quinone compound–thiol system and the rate constants of the elementary stages were determined based on this mechanism.

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