ISSN 0023-1584, Kinetics and Catalysis, 2015, Vol. 56, No. 3, pp. 276–284. © Pleiades Publishing, Ltd., 2015.
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Mechanism of the Reaction between *N*,*N*′-Diphenyl-1,4-Benzoquinone Diimine and Thiophenol in *n*-Propanol

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Received July 16, 2014

Abstract—We studied the kinetics of the reaction between *N*,*N*′-diphenyl-1,4-benzoquinone diimine and thiophenol in *n*-propanol at 343 K and compared the results with the same data for the chlorobenzene medium. The replacement of chlorobenzene with *n*-propyl alcohol increases the reaction rate by one order of magnitude. The order of the reaction with respect to thiophenol was determined to be 1.0 in both solvents, and the order of the reaction with respect to quinone diimine decreases from 1.5 to 1.2 on passing from chlorobenzene to *n*-propanol. In contrast to the reaction in chlorobenzene, where the radical chain mechanism is realized, the reaction in *n*-propanol simultaneously proceeds via a radical chain channel and a heterolytic channel. In the absence of an initiator and at equal reactant concentrations of ~10^{-4} mol/L, the reaction rates in both pathways are commensurable. The chain reaction is characterized by short chains whose length is a few units. Chain generation in the absence of an initiator occurs by the direct bimolecular reaction between the reactants, whose rate constant in *n*-propanol is one order of magnitude higher than that in chlorobenzene, which is explained by the high polarity of the transition state in this endothermic homolytic reaction. The reaction mechanism was proposed, and, for this mechanism, the rate constants of elementary steps were determined.

DOI: 10.1134/S0023158415030222

In recent years, due to environmental pollution and wide application of pharmaceuticals, increasingly high amounts of quinone compounds, such as quinone and quinone imines, enter human and animal bodies. As an example, we shall mention a series of antitumor antibiotics, as well as the commonly used analgetic paracetamol, whose main metabolite is highly toxic *N*-acetyl-1,4-benzoquinone monoimine [1]. One of the main causes of the toxicity of quinone compounds is their capability of reacting with the S–H groups of sulfur-containing biosubstances (cysteine, glutathione, and other compounds acting as bioantioxidants [2]), which results in their irreversible binding ("desulfurization" of body), giving rise to serious diseases [3–9]. For this reason, the reactions of quinone compounds with thiols attract biochemists' interest.

It was believed for a long time that the mentioned reactions proceed via the nucleophilic 1,4-addition of thiol to the cyclohexadiene ring of quinone or quinone imine [10–13]. This view relied mainly on the data on the product composition in these reactions (mostly performed in polar mediums), and, until recently, have been weakly confirmed by kinetic data [14, 15]. Therefore, it is quite natural that recent kinetic studies showed that some reactions of quinone compounds with thiols (in particular, 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 [16], as well as with thiophenol (PhSH) and *n*-decylthiol $C_{10}H_{21}SH$ [17]) proceed not via the ionic mechanism, but via radical one and even via a radical chain one.

Knowledge of the mechanism of the reactions of quinone compounds with thiols is necessary to predict the reaction path and rate under different conditions. Of special interest are data on how the reaction kinetics and mechanism change on passing from low-polarity solvents to polar proton-donor ones. Taking into account this fact, using the reaction between *N*,*N*-diphenyl-1,4-benzoquinone diimine and thiophenol as an example, we studied, in detail, the kinetics and mechanism of said reactions in chlorobenzene, as well as in *n*-propanol, which is closer in its properties to the medium where biochemical processes occur. When selecting *n*-propanol we took into consideration that water and alcohol–water mixtures are not suitable for the purposes of our study due to very low solubilities of the reactants and initiators therein. Methanol and ethanol, which are closest to water in their properties, are also unsuitable due to their low boiling points.

The results obtained in the study of the reaction between *N*,*N*′-diphenyl-1,4-benzoquinone diimine and thiophenol in chlorobenzene are presented in [18]. In this work, we studied the kinetics of this reaction in *n*-propanol.

EXPERIMENTAL

The reaction of QDI with PhSH was studied by kinetic spectrophotometry as in the case of chlorobenzene [18]. The experiments were performed at $T = 343 \pm 0.2$ K in an argon atmosphere in quartz bubbler-type reactor cells (with a volume of 6.5 or 8.5 mL and an optical path length of 2.0 cm) integrated in Specord UV-VIS and Specord M 40 spectrophotometers (Carl Zeiss, GDR). The error in light absorbance and concentration measurements was not larger than 2%. The course of the reaction was monitored as QDI consumption by recording, at 1-s intervals, the absorbance (with data output on a PC screen) for the absorption band of QDI in the visible region. The extinction coefficients of QDI were determined from the absorbance at the early stages of the reaction. The ε values determined are close to those obtained earlier in chlorobenzene [19] (ε, L mol^{-1} cm^{-1}: 6560 at 449 nm, 3440 at 500 nm, and 1370 at 526 nm). Preliminary, experiments in which the spectrum was recorded at regular intervals during the reaction were performed. The invariability of the spectra indicates that only quinone diimine absorbs light at the analytical wavelength during the experiment. Afterwards, the reaction kinetics was studied by monitoring at the specified wavelength.

The initiator, viz., tetraphenylhydrazine $(C_6H_5)_2N–N(C_6H_5)_2$ (TPH), was synthesized according to the procedure described in [18]. In our calculations, the initiation rate constant k_i (TPH) = 1.96×10^{-4} s^{-1} in chlorobenzene [20] was used. This did not resulted in a large error, since the experiments on the decomposition of TPH in a number of solvents (decane, dimethyl sulfoxide, butanol, and *N*,*N*-dimethylformamide) showed that the solvent nature has only a weak effect on k_i(TPH). Quinone diimine was synthesized according to the procedure described in [21] by the oxidation of *N*,*N*′-diphenyl-1,4-phenylene diamine (**H_2QDI**) with potassium permanganate in acetone. The true concentrations of the reactants and additives at 343 K were calculated taking into account a thermal expansion coefficient of 1×10^{-3} K^{-1}. Thiophenol PhSH (Aldrich, ≥99%) was used as received. *n*-Propyl alcohol (Aldrich, ACS reactants, 99.5%) was purifried by distillation b.p. 97.0°C) and was dried by passing it at a flow rate of 50–70 mL/h through a 8-cm-thick bed of molecular sieve 4 Å (Sigma-Aldrich, 4–8 mesh) in a glass column (20 × 2.5 cm).

The kinetics of the reaction was studied using the initial consumption rate of quinone diimine, w_{QDI}. To determine w_{QDI}, the experimental QDI consumption curves were fitted to an empirical equation that agreed good with the experimental data at the initial reaction steps (5–10 min). The most suitable function for this purpose was

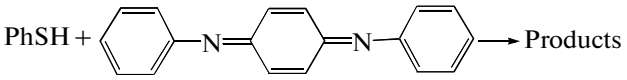
$$[QDI] = a_1 e^{-b_1 t} + a_2 e^{-b_2 t} + c,$$

where a_1, a_2, b_1, b_2, and c are constants (parameters) determined by iterative methods; as a rule, $c = 0$. In most cases, the above-mentioned function described, with a high accuracy, the experimental curves not only at the initial steps but also during the entire run, whose duration was sometimes several hours. The determined values of the parameters were used to calculate w_{QDI} via the formula

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

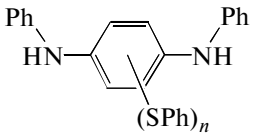
RESULTS AND DISCUSSION

The reaction of QDI with PhSH can be written schematically as follows:



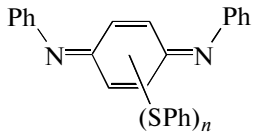
QDI

The reaction products are central ring-thiosubstituted *N*,*N*′-diphenyl-1,4-phenylene diamines (**I**), *N*,*N*′-diphenyl-1,4-phenylene diamine (H_2QDI), disulfide PhSSPh, and thiosubstituted quinone diimines (**II**) [10–13]. Compounds **I** form first, and then they transform under the action of the initial QDI or other oxidizing agents into the corresponding substituted quinone diimines **II** [22–24]. Most experiments were performed at $[PhSH]_0 \gg [QDI]_0$; therefore, one can assume that onlu monothiosubstituted *N*,*N*′-diphenyl-1,4-phenylene diamine **I** ($n = 1$) forms at the initial stages.



$n = 1–4$

(I)



$n = 1–4$

(II)

Reaction Kinetics in the Absence of an Initiator

The replacement of chlorobenzene with *n*-propanol resulted in an about tenfold increase in the reaction rate. High reaction rates often cause inconveniences in recording the kinetics; for this reason, the experiments were usually performed at relatively low concentrations of the reactants. To determine the reaction orders, we plotted w_{QDI} against the reactant concentrations in a set of experiments at a constant concentration of one component and a variable concentration of the other one. At $[QDI]_0$ = const, the dependences of w_{QDI} on $[PhSH]_0$ are linear, all straight lines within the experimental accuracy, and pass through the origin of coordinates (Fig. 1).

$$w_{QDI} = (k \times [QDI]_0^{n_{QDI}}) \times [PhSH]_0 = B[PhSH]_0. \quad (1)$$

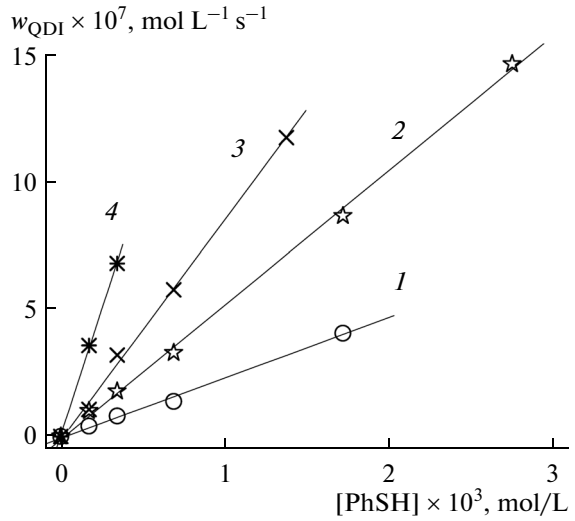


Fig. 1. Determination of the reaction orders with respect to PhSH at different (but constant in a given experimental series) concentrations of QDI × 10^5 (mol/L): (*1*) 4.30, (*2*) 8.60, (*3*) 13.0, and (*4*) 26.0. *n*-Propanol, 343 K.

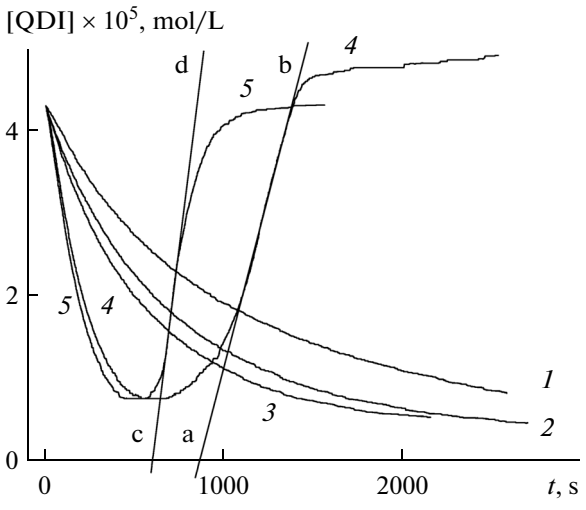


Fig. 2. Translated on QDI concentration curves of change in absorbance at 449 nm (ν= 22260 cm^{-1}) in the reaction of QDI with PhSH at different initiation rates $w_i \times 10^8$, (mol L^{-1} s^{-1}): (*1*) 0, (*2*) 1.52, (*3*) 3.80, (*4*) 15.2, and (*5*) 28.6. [QDI] = 4.30×10^{-5} mol/L, [PhSH] = 1.72×10^{-4} mol/L, *n*-propanol, 343 K.

These data suggest that the reaction is first-order with respect to PhSH:

$$n_{PhSH} = 1.0.$$

In the determination of the reaction order with respect to QDI (by plotting the coefficients *B* of Eq. (1) as a function of the QDI concentration), it was found that the experimental data are well approximated by the power function:

$$B = k[QDI]_0^{n_{QDI}}, \quad (2)$$

where *k* and n_{QDI} are coefficients determined by iterations:

$$k = 38.1 \pm 2.1, \quad n_{QDI} = 1.19 \pm 0.01.$$

An earlier study of the reaction between QDI and PhSH in chlorobenzene gave the value $n_{QDI} \approx 1.5$ [18]. As can be seen, the substitution of *n*-propanol for chlorobenzene results in a decrease in the reaction order with respect to QDI from 1.5 to 1.2. The noninteger order with respect to QDI suggests that the reaction between QDI and PhSH proceeds via a complicated mechanism in both solvents.

According to Eqs. (1) and (2), the results of all our experiments in the absence of an initiator (more than 20 runs) fall close to a common straight line:

$$w_{QDI} = (39.7 \pm 0.4)[QDI]_0^{1.2}[PhSH]_0$$

with a correlation coefficient of $r = 0.999$. The w_{QDI} values in this relationship vary from 0 to 1.5×10^{-6} mol L^{-1} s^{-1}.

Initiation Kinetics of the Reaction

It follows from Fig. 2 that the reaction rate is higher in the presence of the initiator. In *n*-propanol, the effect of the initiator on w_{QDI} is significantly weaker than in chlorobenzene. For this reason, the effect of w_i on w_{QDI} was studied at initiation rates that are 1–1.5 order of magnitude greater than w_i in the experiments involving chlorobenzene.

A distinctive feature of the initiated reaction kinetics in *n*-propanol is the presence of the second reaction step, in which an increase in absorbance is observed (Fig. 2, curves *3–5*). During these experiments, it is seen (Fig. 3) in the absorption spectra that the absorption is caused by an accumulating product other than QDI. The spectrum of this product is close to that of QDI, although the maximum of the first absorption band undergoes a small bathochromic shift. It also follows from Fig. 3 (curves *1, 9*) and Fig. 2—absorption at the beginning of the run, caused by the presence of QDI, is close in its intensity to that in the terminal, nearly horizontal segments of curves *4* and *5*, where the product absorbs—that the extinction coefficients of the product and QDI are similar. Since the aim of our work was to study the kinetics of the reaction between QDI and PhSH, no isolation and identification of the reaction product were performed, although from the data presented in Figs 2 and 3 one can draw some important and quite reliable conclusions (see comments below).

The considerably weaker effect of w_i on w_{QDI} is explained by the fact that the reaction of QDI with PhSH in *n*-propanol proceeds via two channels, of which one is not a chain reaction and, therefore, cannot be accelerated by an initiator. As follows from the literature, the second pathway is the heterolytic reaction between the quinone compound and thiol, which, recently, has been confirmed experimentally

by a study of the quinone–thiol system in water at room temperature [15]. This reaction affords the same products as the radical-chain one, but it cannot be accelerated using an initiator. When performing a kinetic analysis, one should take into account that the heterolytic reaction is first-order with respect to each component [14, 25].

Reaction Mechanism

An analysis of the data obtained shows that the kinetic regularities of the reaction in *n*-propanol agree well with a mechanism that is close to the mechanism proposed earlier for the chain reaction of QDI with PhSH in chlorobenzene [18], but supplemented with an additional step, namely, the nonchain reaction between the reactants:

$$\mathrm{QDI + PhSH \rightarrow (I, } n = 1), \qquad k_{1nc} \quad (\mathbf{I_{nc}})$$

$$\mathrm{I \longrightarrow Ph_2N^{\bullet} \xrightarrow{+PhSH} PhS^{\bullet}}, \qquad k_i \quad \text{(i)}$$

$$\mathrm{QDI + PhSH \rightarrow HQDI^{\bullet} + PhS^{\bullet}}, \; k_{1bi} \quad (\mathbf{I_{bi}})$$

$$\mathrm{HQDI^{\bullet} + PhSH \rightarrow H_2QDI + PhS^{\bullet}},$$

$$\mathrm{PhS^{\bullet} + QDI \leftrightarrow RA^{\bullet} \rightarrow AmN^{\bullet}Ph}, \qquad k_2 \quad \text{(II)}$$

$$\mathrm{AmN^{\bullet}Ph + PhSH \rightarrow (I, } n = 1) + \mathrm{PhS^{\bullet}}, \; k_3 \quad \text{(III)}$$

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

where $RA^{\bullet}$ is a radical adduct.

This scheme has no initiation step ($\mathbf{I_{tri}}$) proceeding as a third-order reaction

$$\mathrm{PhSH + QDI + PhSH \rightarrow PhS^{\bullet} + H_2QDI + PhS^{\bullet}}, \qquad k_{1tri}\,(\mathbf{I_{tri}})$$

which plays an important role in the mechanism of the reaction between QDI and PhSH in chlorobenzene [18].

The conclusion about the insignificant role of this reaction in *n*-propanol follows from the results of the kinetic processing of experimental data within the scheme taking also into account the above-mentioned reaction ($\mathbf{I_{tri}}$). A negligible role of this reaction is likely due to the stronger solvation of the reactants compared to chlorobenzene.

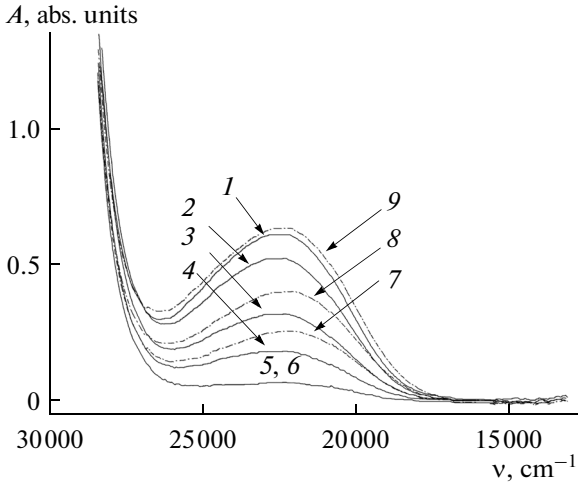
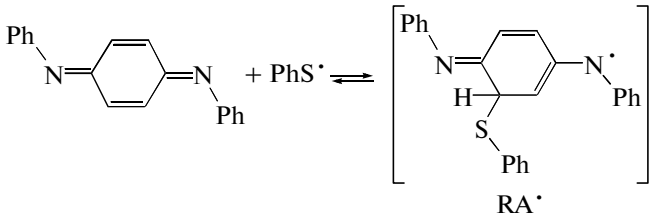


Fig. 3. Change in the absorption spectra in the reaction of QDI with PhSH in the presence of the initiator (cf. curve *4* in Fig. 2). Reaction time, s: (*1*) 0, (*2*) 67, (*3*) 189, (*4*) 309, (*5*) 545, (*6*) 878, (*7*) 1367, (*8*) 1487, and (*9*) 2530. $[QDI] = 4.30 \times 10^{-5}$ mol/L, $[PhSH] = 1.72 \times 10^{-4}$ mol/L, *n*-propanol, 343 K, $w_i = 1.52 \times 10^{-7}$ mol L^{-1} s^{-1}.

According to the scheme, in the absence of an initiator the formation of the primary phenylthiyl $C_6H_5S^{\bullet}$ ($PhS^{\bullet}$) and 4-anilinodiphenylaminyl C_6H_5–$N^{\bullet}$–C_6H_4–NH–C_6H_5 (**HQDI$^{\bullet}$**) radicals occurs via a bimolecular reaction ($\mathbf{I_{bi}}$) between QDI and PhSH. Subsequently, the $HQDI^{\bullet}$ radicals undergo radical exchange with PhSH to be replaced rapidly with $PhS^{\bullet}$ radicals, which are one of the two kinds of chain carrier radicals in step (II) of the reversible reaction of $PhS^{\bullet}$ with the cyclohexadiene ring of QDI yielding the radical adduct $RA^{\bullet}$:

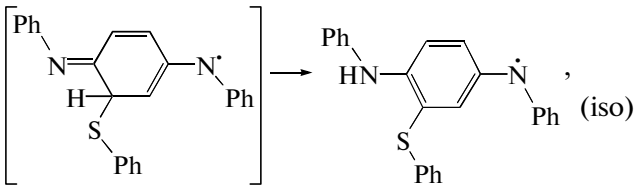


(a, f)

where (a) is the adduct formation and (f) is its fragmentation.

The $RA^{\bullet}$ formation step is analogous to the known reversible reaction of thiyl radicals with unsaturated carbon–carbon bonds of olefins [26]. However, the subsequent transformations of the radical adducts of these two reactions are different, because, in the case of the $RA^{\bullet}$ adduct, it is necessary

that the adduct isomerize into the diarylaminyl radical AmN$^{\bullet}$Ph:[1]



RA$^{\bullet}$ AmN$^{\bullet}$Ph

which is the second kind of chain carrier radicals in step (III). Note that no such isomerization of radicals occurs in the similar reaction between thiol and olefins.

The expression for the rate of AmN$^{\bullet}$Ph accumulation (step (II), w_{AmNPh}) depends on the ratio between the rate constants of RA$^{\bullet}$ fragmentation k_{f} and isomerization k_{iso}. An important point is that in this case w_{AmNPh} can be expressed as the product of the QDI and PhS$^{\bullet}$ concentrations. For example, if $k_{\mathrm{iso}} \gg k_{\mathrm{f}}$, then

$$w_2 = k_2[\mathrm{QDI}][\mathrm{PhS}^{\bullet}] = w_{\mathrm{AmNPh}} = k_{\mathrm{iso}}[\mathrm{RA}^{\bullet}] = k_{\mathrm{a}}[\mathrm{QDI}][\mathrm{PhS}^{\bullet}] \quad \text{and } k_2 = k_{\mathrm{a}}. \tag{3}$$

If $k_{\mathrm{f}} \gg k_{\mathrm{iso}}$, then $[\mathrm{RA}^{\bullet}] = (k_{\mathrm{a}}/k_{\mathrm{f}})\,[\mathrm{QDI}][\mathrm{PhS}^{\bullet}]$ and $w_2 = k_2[\mathrm{QDI}][\mathrm{PhS}^{\bullet}] = w_{\mathrm{AmNPh}} = k_{\mathrm{iso}}[\mathrm{RA}^{\bullet}] = (k_{\mathrm{iso}}k_{\mathrm{a}}/k_{\mathrm{f}})\,[\mathrm{QDI}][\mathrm{PhS}^{\bullet}]$,

$$\text{i.e., } k_2 = k_{\mathrm{iso}}k_{\mathrm{a}}/k_{\mathrm{f}}. \tag{3a}$$

For further analysis, let us take into account the following remark. The chain length of the reaction between QDI and PhSH in chlorobenzene is only ~10 units [18]. Due to the solvation of the reactants and/or radicals and intermediates, the chain length in *n*-propanol can be much less; for this reason, when analyzing the data for *n*-propanol, one should take into account the consumption of QDI in both the chain propagation step (II) and radical generation step ($\mathrm{I_{bi}}$). Then, taking into account the nonchain reaction between components ($\mathrm{I_{nc}}$), we obtain the following equation:

$$w_{\mathrm{QDI}} = k_{1\mathrm{nc}}[\mathrm{QDI}][\mathrm{PhSH}] + k_{1\mathrm{bi}}[\mathrm{QDI}][\mathrm{PhSH}] + k_2[\mathrm{QDI}][\mathrm{PhS}^{\bullet}]. \tag{4}$$

From the stationarity condition of the reaction,

$$w_{\mathrm{i}} + 2k_{1\mathrm{bi}}[\mathrm{QDI}][\mathrm{PhSH}] = 2k_4[\mathrm{PhS}^{\bullet}]^2$$

we obtain the formula for the concentration of PhS$^{\bullet}$ radicals:

$$[\mathrm{PhS}^{\bullet}] = \left(\frac{0.5w_{\mathrm{i}} + k_{1\mathrm{bi}}[\mathrm{QDI}][\mathrm{PhSH}]}{k_4}\right)^{1/2}, \tag{5}$$

[1] We are currently analyzing this reaction by quantum chemical methods.

Substituting this expression into (4), we obtain

$$w_{\mathrm{QDI}} = (k_{1\mathrm{bi}} + k_{1\mathrm{nc}})[\mathrm{QDI}][\mathrm{PhSH}] + \frac{k_2}{k_4^{1/2}}[\mathrm{QDI}]\{0.5w_i + k_{1\mathrm{bi}}[\mathrm{QDI}][\mathrm{PhSH}]\}^{1/2}. \tag{6}$$

In the absence of an initiator, Eq. (6) reduces to

$$w_{\mathrm{QDI}} = (k_{1\mathrm{bi}} + k_{1\mathrm{nc}})[\mathrm{QDI}][\mathrm{PhSH}] + \frac{k_2k_{1\mathrm{bi}}^{1/2}}{k_4^{1/2}}[\mathrm{QDI}]^{3/2}[\mathrm{PhSH}]^{1/2}. \tag{7}$$

Let us consider Eq. (7) in detail taking into account the numeric values of $(k_{1\mathrm{bi}} + k_{1\mathrm{nc}})$ and $\frac{k_2k_{1\mathrm{bi}}^{1/2}}{k_4^{1/2}}$ given below. The reactant concentrations in the determination of n_{PhSH} were such that the values of the multiplying factor $\frac{k_2k_{1\mathrm{bi}}^{1/2}}{k_4^{1/2}}[\mathrm{QDI}]^{3/2}$ in the second summand preceding $[\mathrm{PhSH}]^{1/2}$ were significantly smaller than the multiplying factor $(k_{1\mathrm{bi}} + k_{1\mathrm{nc}})[\mathrm{QDI}]$ before [PhSH] in the first term of the sum. The value of the second summand itself in Eq. (7) was smaller than value of the first summand. Under these conditions, $w_{\mathrm{QDI}} \sim (k_{1\mathrm{bi}} + k_{1\mathrm{nc}})[\mathrm{QDI}][\mathrm{PhSH}] = \mathrm{const}[\mathrm{PhSH}]$; i.e., one can determine experimentally only the first order with respect to PhSH. In the determination of the reaction orders with respect to QDI, the multipliers preceding $[\mathrm{QDI}]^{3/2}$ and [QDI] in the first and second terms of the sum in Eq. (7) differed not so greatly, and, therefore, the experimental order of the reaction with respect to QDI could be expected to be in the range between 1 and 1.5 ($1.5 > n_{\mathrm{QDI}} > 1$), which was indeed observed experimentally.

To fit Eq. (7) to experimental data, let us rearrange it into

$$\frac{w_{\mathrm{QDI}}}{[\mathrm{QDI}][\mathrm{PhSH}]} = (k_{1\mathrm{bi}} + k_{1\mathrm{nc}}) + \frac{k_2k_{1\mathrm{bi}}^{1/2}}{k_4^{1/2}}\left(\frac{[\mathrm{QDI}]}{[\mathrm{PhSH}]}\right)^{1/2}. \tag{8}$$

As is shown in Fig. 4, the resulting equation agrees satisfactorily with the experimental data. From the ordinate intercept and the slope of the straight line, we find

$$k_{1\mathrm{bi}} + k_{1\mathrm{nc}} = 5.1 \pm 0.3\ \mathrm{L\ mol^{-1}\ s^{-1}}, \tag{8a}$$

$$\frac{k_2k_{1\mathrm{bi}}^{1/2}}{k_4^{1/2}} = 2.6 \pm 0.4\ \mathrm{L\ mol^{-1}\ s^{-1}}. \tag{8b}$$

Assuming that, in the experiments performed in the presence of the initiator, the latter is the main source of radicals, i.e., $w_{\mathrm{i}} \gg k_{1\mathrm{bi}}[\mathrm{QDI}][\mathrm{PhSH}]$, we obtain the following equation from Eq. (6):

$$w_{\mathrm{QDI}} = (k_{1\mathrm{bi}} + k_{1\mathrm{nc}}) \times [\mathrm{QDI}][\mathrm{PhSH}] + \frac{k_2}{(2k_4)^{1/2}}[\mathrm{QDI}]w_i^{1/2}. \tag{9}$$

Table 1. Reaction rate w_{QDI} at different initiation rates w_i and coefficients E and F for the plot of w_{QDI} against $w_i^{1/2}$ (Eq. 9a) for the experimental series at $[PhSH]_0 = 1.72 \times 10^{-4}$ mol/L

$w_i \times 10^7$, mol L^{-1} s^{-1}	$w_i^{1/2} \times 10^4$, (mol L^{-1}s^{-1})$^{1/2}$	$w_{QDI} \times 10^7$, mol L^{-1}s^{-1}	$E \times 10^8$, mol L^{-1}s^{-1}	$F \times 10^4$, (mol L^{-1}s^{-1})$^{1/2}$
$[QDI]_0 = 4.30 \times 10^{-5}$ mol/L				
0	0	0.41		
0.152	1.23	0.58		
0.380	1.95	0.71	3.7 ± 0.57	2.0 ± 0.2
1.520	3.90	1.23		
2.090	4.57	1.27		
$[QDI]_0 = 8.60 \times 10^{-5}$ mol/L				
0	0	1.01		
0.152	1.23	1.45		
0.760	2.76	2.02	9.7 ± 0.5	4.0 ± 0.2
1.520	3.90	2.48		
2.090	4.57	2.87		
$[QDI]_0 = 1.30 \times 10^{-4}$ mol/L				
0	0	1.07		
0.152	1.23	1.55	9.4 ± 1.7	6.0 ± 0.7
0.760	2.76	2.41		
1.520	3.90	3.42		

According to Eq. (9), for the experimental series with variable w_i and constant QDI and PhSH concentrations, the following linear relationship must be fulfilled:

$$w_{QDI} = E + Fw_i^{1/2}, \quad (9a)$$

$$\text{where } E = (k_{1bi} + k_{1nc})[QDI][PhSH], \quad (9b)$$

$$F = \frac{k_2}{(2k_4)^{1/2}}[QDI]. \quad (9c)$$

The corresponding experimental data are given in Table 1. Based on these data, we constructed linear plots of w_{QDI} versus $w_i^{1/2}$ (9a), from which the parameters E and F were determined as the ordinate intercepts and the slopes of these straight lines (Table 1). Using the found values of E and F, we plotted E versus [QDI][PhSH] (9b), as well as F versus [QDI] (9c) (in both cases the origin of coordinates (0, 0) was added to the experimental points). From the slopes of these straight lines, we obtained the following values:

$$k_{1bi} + k_{1nc} = 4.6 \pm 1.2 \text{ L mol}^{-1} \text{ s}^{-1}, \quad (10)$$

$$\frac{k_2}{(2k_4)^{1/2}} = 4.58 \pm 0.04 \text{ (L mol}^{-1} \text{ s}^{-1})^{1/2}. \quad (11)$$

The value of $(k_{1bi} + k_{1nc})$ found in this way agrees within the experimental accuracy with the above value (8a), which was obtained by processing of experimental data acquired in the absence of an initiator.

A comparison between the value $k_2/(2k_4)^{1/2} = 4.58 \pm 0.04$ (L mol^{-1} s^{-1})$^{1/2}$ obtained in alcohol and the value $k_2/(2k_4)^{1/2} = 11.8 \pm 0.04$ (L mol^{-1} s^{-1})$^{1/2}$ for chlorobenzene [18] suggests that the above-mentioned kinetic parameter decreases by a factor of 2.6 on passing from chlorobenzene to *n*-propanol. This result possibly indicates a non-elementary character of step (II) in the above scheme and can also be due to the formation of hydrogen-bonded complexes between QDI and *n*-propanol and/or to the solvent effect on the rate constants of RA$^{\cdot}$ fragmentation and isomerization.

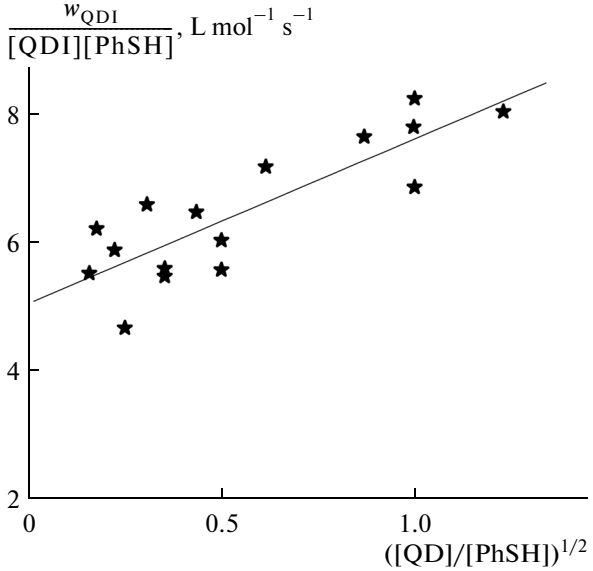


Fig. 4. Fitting the experimental data obtained in the absence of the initiator to Eq. (8).

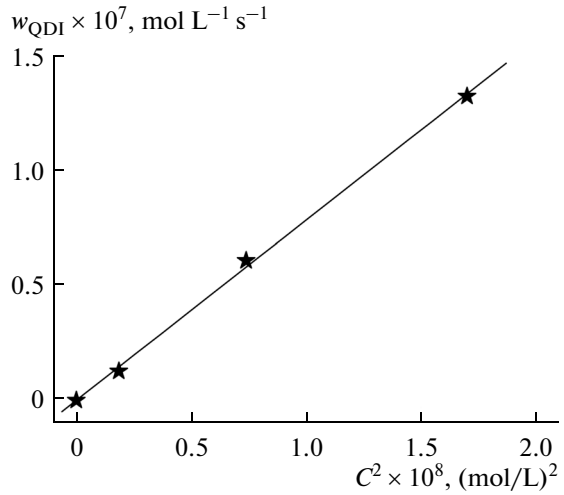


Fig. 5. Results of the experiments performed at equal reactant concentrations, $[QDI]_0 = [PhSH]_0 = C$, in the w_{QDI}–C^2 coordinates of Eq. (13).

From relationships (11) and (8b), we obtain

$$k_{1bi} = 0.16 \pm 0.05 \text{ L mol}^{-1} \text{ s}^{-1}. \quad (12)$$

In chlorobenzene, k_{1bi}(343 K) is 0.014 ± 0.002 L mol^{-1} s^{-1} [18]; i.e., when substituting *n*-propanol for chlorobenzene, the rate constant of radical formation in the bimolecular reaction of QDI with PhSH increases by one order of magnitude. Apparently, this result suggests that the polarity of the transition state of the endothermic reaction (I_{bi}) is considerably higher than that of the starting reactants. A significant acceleration of endothermic radical reactions on passing to polar solvents (in particular, the bimolecular decomposition of molecules into radicals) has been noted in the literature in many cases. The cause of the accelerating effect of polar solvents in these reactions is that, due to the stronger solvation of polar transition states in polar solvents, the activation energy of the reaction increases (see [2, chapter 4; 27–29]), which results in an increase in the rate constant. Taking into account Eqs. (8a) and (12), we obtain

$$k_{1nc} = 4.94 \pm 0.35 \text{ L mol}^{-1} \text{ s}^{-1}. \quad (12a)$$

Experiments at Equal Concentrations of the Reactants

Additional information was obtained in the experiments using the reactants at equal concentrations.

According to Eq. (7), at $[QDI]_0 = [PhSH]_0 = C$ the following equation is true for the reaction rate:

$$w_{QDI} = \left(k_{1bi} + k_{1nc} + \frac{k_2 k_{1bi}^{1/2}}{k_4^{1/2}}\right) C^2. \quad (13)$$

It follows from Eq. (13) that the data obtained in these experiments are linearizable in the w_{QDI}–C^2 coordinates. The resulting straight line must intersect the origin of coordinates, and the slope of this line must be equal to the sum of the values of the parameters in Eqs. (8a) and (8b). The processing of the data obtained in the experiments with equal concentrations of the reactants shows that the experimental points fall close to the straight line intersecting the origin of coordinates (Fig. 5). From the slope of this line, we determine

$$k_{1bi} + k_{1nc} + \frac{k_2 k_{1bi}^{1/2}}{k_4^{1/2}} = 7.85 \pm 0.19 \text{ L mol}^{-1} \text{ s}^{-1},$$

which is in agreement with the expected value, namely, the sum of the values in Eqs. (8a) and (8b).

The resulting rate constants for the most important steps of the scheme allow calculation of the rates of chain and nonchain reaction pathways, as well as the chain length. The corresponding data are given in Table 2. It can be seen in some cases that, due to the experimental errors, the calculated rates of the reaction proceeding via the chain pathway, w_c, are smaller than $w_{i(\Sigma)}$ and even have negative values.

Remarks on the Accumulation of the Colored Product (Fig. 2)

The colored products of reaction of QDI with PhSH are thiosubstituted quinione imines **II**, whose spectra are close to those of the starting unsubstituted quinone imine [13, 23]. For this reason, one can assume that the increase in absorbance in Fig. 2 is caused by the accumulation of monothiosubstituted quinone diimine II ($n = 1$).

An argument in favor of this assumption is the fact that the product accumulation starts not immediately, but at the end of a prolonged induction period (Fig. 2). This excludes the possibility of product formation by the reaction between the initiator's radical $Ph_2N^{\bullet}$ and the radical intermediate $RA^{\bullet}$, which is the precursor of the product:

$$RA^{\bullet} + Ph_2N^{\bullet} \text{—}\times\rightarrow \text{II } (n = 1) + Ph_2NH,$$

otherwise, there would be no induction period. Estimations showed that the accumulation of the colored product starts only after the complete consumption of thiophenol. Indeed, taking into account the stoichiometry of the reaction between QDI and PhSH (1 : 1), we deduce that, after the end of the initial periods of QDI consumption (curves *4*, *5*), part of the thiophenol PhSH, at a concentration of 4.3×10^{-5} mol/L, will be bound in the form of monosubstituted *N*,*N*'-diphenyl-1,4-phenylene diamine I ($n = 1$) and the other part, at a concentration of $(1.72 \times 10^{-4}) - (4.3 \times 10^{-5}) = 1.29 \times 10^{-4}$ mol L^{-1}, will be present in the reaction mixture and will be able to react with radicals of the initiator:

$$PhSH + Ph_2N^{\bullet} \rightarrow PhS^{\bullet} + Ph_2NH,$$

$$PhS^{\bullet} + PhS^{\bullet} \rightarrow PhSSPh.$$

Complete PhSH consumption requires a time of $(1.29 \times 10^{-4})/w_i = 850$ s (curve *4*) or 450 s (curve *5*). It follows from Fig. 2 that the resulting rough esti-

Table 2. Reaction rates for the chain and nonchain pathways and the chain length in the chain reaction

$[QDI]_0 \times 10^5$	$[PhSH]_0 \times 10^4$	$w_{QDI} \times 10^8$	$w_{i(TPH)} \times 10^8$	$w_{i(0)} \times 10^8$*	$w_{i(S)} \times 10^8$**	$w_{nc} \times 10^8$***	$w_c \times 10^8$****	Chain length*****
mol/L		mol L^{-1} s^{-1}						
4.3	6.88	13.8	0	0.95	0.95	14.6	–	–
	3.44	8.1	0	0.47	0.47	7.3	7.8	1.7
	1.72	4.1	0	0.24	0.24	3.7	0.47	2.0
	1.72	7.1	3.8	0.24	4.0	3.7	3.4	–
	1.72	12.3	15.2	0.24	15.4	3.7	8.6	–
8.6	6.88	33.1	0	1.89	1.89	29.2	3.8	2.0
	3.44	17.8	0	0.95	0.95	14.6	3.2	3.4
	1.72	10.1	0	0.47	0.47	7.3	2.8	5.9
	1.72	14.5	1.5	0.47	1.97	7.3	7.2	3.6
	1.72	20.2	7.6	0.47	8.07	7.3	12.9	1.6
	1.72	24.8	15.2	0.47	15.7	7.3	17.5	1.1
13.0	6.88	57.9	0	2.86	2.86	44.2	13.7	4.8
	3.44	32.1	0	1.43	1.43	22.1	10.0	7.0
	1.72	10.7	0	0.72	0.72	11.0	–	–
	1.72	15.5	1.5	0.72	2.22	11.0	4.5	2.0
	1.72	24.1	7.6	0.72	8.32	11.0	13.0	1.6
	1.72	34.2	15.2	0.72	15.9	11.0	23.2	1.5
4.3	4.3	1.27	0	0.059	0.059	0.91	0.35	6.0
8.6	8.6	6.09	0	0.24	0.24	3.7	2.4	10.3
13.0	13.0	13.3	0	0.54	0.54	8.4	4.8	8.9

* $w_{i(0)} = 2k_{1bi}[QDI][PhSH]$.
** $w_{i(S)} = w_{i(TPH)} + w_{i(0)}$
*** $w_{nc} = k_{1nc}[QDI][PhSH]$.
**** $w_c = w_{QDI} - w_{nc}$.
***** Chain length $= w_c/w_{i(S)}$.

mates agree quite satisfactorily with experimental data.

After the consumption of PhSH, the $Ph_2N^{\cdot}$ radicals start to attack thiosubstituted *N*,*N*'-diphenyl-1,4-phenylene diamine I ($n = 1$) as a less powerful hydrogen donor, which results in the formation of thiosubstituted quinone diimine II ($n = 1$):

$$\text{I } (n = 1) + Ph_2N^{\cdot} \rightarrow AmN^{\cdot}Ph + Ph_2NH,$$

$$AmN^{\cdot}Ph + AmN^{\cdot}Ph \rightarrow \text{I } (n = 1) + \text{II } (n = 1).$$

Drawing tangents ab and cd to curves *4* and *5* at the points of inflection in their ascending segments and assuming that the extinction coefficient of product II ($n = 1$) at the analytical wavelength is equal to that of QDI (cf. the absorbances at the start of the reaction and in the horizontal segments of curves *4* and *5*), one can calculate the accumulation rates of product II ($n = 1$) at the inflection points w_{inflec}, from which the values of w_{inflec}/w_i are determined:

curve *4* $w_{inflect} = 8.5 \times 10^{-8}$ mol L^{-1} s^{-1} and $w_{inflect}/w_i = 0.56$,

curve *5* $w_{inflect} = 1.8 \times 10^{-7}$ mol L^{-1} s^{-1} and $w_{inflect}/w_i = 0.63$.

The resulting w_{inflec}/w_i values are close to 0.5, which would be expected from the reaction stoichiometry.

These data serve as a kinetic confirmation for the literature conceptions of the product formation sequence in the reaction of quinone compounds with thiols.

Thus, the comparison of the present results with the data obtained for chlorobenzene [18] suggests that the solvent nature has a strong effect on the kinetics and mechanism of the reaction between QDI and PhSH. Passing from chlorobenzene to *n*-propanol not only an increases the reaction rate by one order of magnitude but also gives birth to a new pathway, which

appears to be related with the heterolytic nucleophilic addition of thiol to quinone imine known in the literature. The change from the homolytic mechanism of the reaction to the heterolytic one, depending on the polarity and solvating power of the solvent, is well known. In *n*-propyl alcohol, depending on the reactant concentrations and on the presence of an initiator, both the homolytic chain reaction and the heterolytic mechanism can become dominant. At equal reactant concentrations and in the absence of an initiator, the reaction rates by the two channels are similar. The chain reaction in *n*-propanol is characterized by the formation of short chains that are slightly longer than one unit, and only at equal concentrations of the reactants does the chain length reach approximately 10 units.

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Translated by K. Utegenov