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CHEMICAL KINETICS
AND CATALYSIS

Effect of Propanol-1 on the Reaction between Thiophenol and *N,N'*-Diphenyl-1,4-Benzoquinone Diimine in Chlorobenzene

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Abstract—It is found that the interaction between thiophenol and *N*,*N'*-diphenyl-1,4-benzoquinone diimine proceeds by two routes, one of which is a radical chain reaction and the other is a nonchain reaction between the reagents. The kinetic patterns of the reaction depend substantially on the concentration of propanol-1 in mixtures of it and chlorobenzene. It is shown that at 343 K, replacing chlorobenzene with propanol-1 results in an almost twentyfold increase in the total rate of the reaction. Increasing the concentration of propanol-1 raises the rate of both routes of the reaction, but that of the nonchain route grows more than that of the chain route. It is concluded that increasing the concentration of propanol-1 results in a simultaneous 20–30 times rise in the rate constants of both the stage of radical generation by the reaction between the reagents as well as the rate constant of the nonchain bimolecular reaction, and the chain length of the chain reaction is shortened. When chlorobenzene is replaced with propanol-1, the rate constant of the limiting stage of chain propagation (the reaction of quinone diimine with a phenylthiyl radical) is halved, due to the formation of H complexes between the π system of quinone diimine and the proton of propanol-1.

Keywords: N,*N'*-diphenyl-1,4-benzoquinone diimine, thiophenol, bidirectional reaction, kinetics, mechanism, rate constants, chlorobenzene + propanol-1 binary solvents

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INTRODUCTION

Reactions between thiols and quinoid compounds (quinones and quinone imines) are of great importance in chemistry and biochemistry. Such reactions transform biologically important thiols (e.g., glutathione and cysteine residues of proteins) into compounds with covalent C–S bonds, from which the initial thiols cannot be regenerated. This is one of the main reasons for the high toxicity of quinoid compounds [1–7].

Reactions between thiols and quinone compounds in alcohol and water–alcohol solutions were studied in detail for the first time in [8] through the example of reactions involving 1,4-benzoquinone and its derivatives. Based on the data on the composition and yield of the products, it was concluded that the specified reactions proceed by two routes: (a) an oxidation–reduction transformation of quinone to hydroquinone and thiol to disulfide and (b) via the addition of thiol to the ring of quinone (route (b) predominates). The mechanism of the nucleophilic 1,4-addition of thiol to the cyclohexadiene ring of quinone or quinone imine was later accepted for route (b) [9–12].

The kinetics of the reactions between quinoid compounds and thiols remains poorly studied; until recently, there were very few works [13, 14]. Detailed studies in this field have only just begun through the example of reactions involving quinone imines [15–19]. Literature data stating that the specified reactions proceed by two routes were confirmed from the start. It was a great surprise when the previously unknown radical chain mechanism of one of the routes was proven. It should be noted that the formation of radicals during reactions between quinoid compounds and thiols was noted earlier [20, 21]. These observations did not attract attention, however, and the chain mechanism of the reaction was not considered.

EXPERIMENTAL

Studies show that the rate and composition of the reaction products depend on the nature of the solvent. The rate of the reaction between thiophenol and *N*,*N'*-diphenyl-1,4-benzoquinone diimine thus grows by almost an order of magnitude when chlorobenzene is replaced with propanol-1 [19]. It follows from these data that the kinetic patterns of the reaction in chlorobenzene + propanol-1 binary solvents can be used to obtain additional information on the mechanisms of both routes of the reaction. Considering the great practical importance of these reactions, we decided to consider this problem in more detail in this work.

We therefore analyzed the results from studying the reaction between thiophenol (C_6H_5SH, PhSH) and

Table 1. Rate constants of stages (I), (I_{nc}), and (II); parameter $k_2/(2k_4)^{1/2}$ [19]; and dielectric constants of PhCl + PrOH binary solvents, depending on the molar fraction of PrOH in mixture N_{PrOH}, calculated according to formulas (1) and (2) (T = 343 K, argon bubbling)

N_{PrOH}	k_1	k_{1nc}	$\frac{k_2}{(2k_4)^{1/2}}$	$k_2 \times 10^{-6}$*	ε(298 K)	ε(343 K)
	$L\ mol^{-1}\ s^{-1}$		$(L\ mol^{-1}\ s^{-1})^{1/2}$	$L\ mol^{-1}\ s^{-1}$		
0	0.0084 ± 0.0015	0.25 ± 0.04	10.8 ± 0.3	1.2	5.62	4.89
0.106	0.021 ± 0.0063	0.50 ± 0.06	9.54	1.05	6.78	5.82
0.194	0.0414 ± 0.019	0.96 ± 0.42	8.0 ± 0.13	0.88	7.79	6.60
0.803	0.196 ± 0.081	3.2 ± 1.5	6.87 ± 0.13	0.75	16.5	12.0
1	0.196 ± 0.072	4.8 ± 1.0	5.6 ± 0.65	0.61	20.1	13.7

* Calculations at $k_4 = 6 \times 10^9$ L mol^{-1} s^{-1}; see text.

N,N'-diphenyl-1,4-benzoquinone diimine (C_6H_5–N=C_6H_4=N–C_6H_5, QDI) in mixed chlorobenzene (PhCl) + propanol-1 (PrOH) solvents [17–19]. This study was performed at T = 343 K with argon bubbling, and the kinetic patterns were determined from initial rates w_{QDI} of the consumption of quinone diimine.

Densities d and relative dielectric permeabilities ε of chlorobenzene and propanol-1, which are needed for further investigations, are presented below [22]:

$$d_{PhCl} = 1.10\ \mathrm{kg\ L^{-1}},$$
$$\varepsilon_{PhCl}(298\ \mathrm{K}) = 5.62$$
$$(\partial\varepsilon/\partial T = -0.0168\ \mathrm{K^{-1}}),$$

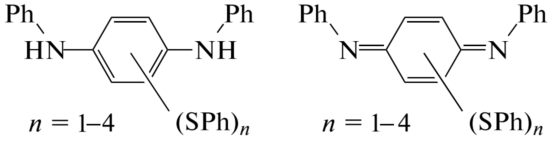
$$d_{PrOH} = 0.800\ \mathrm{kg\ L^{-1}},$$
$$\varepsilon_{PrOH}(298\ \mathrm{K}) = 20.1$$
$$(\partial\varepsilon/\partial T = -0.142\ \mathrm{K^{-1}}).$$

Using these data, the dielectric permeabilities of chlorobenzene ε_{PhCl} and propanol-1 ε_{PrOH} at 343 K,

$$\varepsilon(343\ \mathrm{K}) = \varepsilon(298\ \mathrm{K}) + 45(\partial\varepsilon/\partial T) \quad (1)$$

along with dielectric permeabilities ε of mixtures composed of them,

$$\varepsilon = v_{PhCl}\varepsilon_{PhCl} + v_{PrOH}\varepsilon_{PrOH}, \quad (2)$$



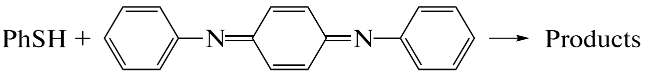
(I) (II)

Scheme 1.

where v_{PhCl} and v_{PrOH} are the volume fractions of chlorobenzene and propanol-1, respectively, calculated in [22] and presented in Table 1.

RESULTS AND DISCUSSION

The reaction between PhSH and QDI proceeds according to the equation



QDI

The products are N,N'-diphenyl-1,4-phenylenediamines (**I**) phenylthio-substituted by the central ring and phenylthio-substituted quinone diimines (**II**), along with N,N'-diphenyl-1,4-phenylenediamine (H_2QDI) and diphenyl disulfide (PhSSPh) [8–10, 23, 24]. Earlier than others, compounds **I** are formed, which are then converted into thiosubstituted quinonediimines **II** under the action of the initial diimine QDI and/or other oxidizing agents. At the initial stages under conditions [PhSH] > [QDI], the reaction does not proceed farther than the formation of monothio-substituted N,N'-diphenyl-1,4-phenylenediamine **I**, n = 1.

The kinetic scheme of the reaction at not deep stages is presented below [16, 17]:

$$\text{Nonchain reaction QDI} + \text{PhSH} \rightarrow (\text{I}, n{=}1),\ k_{1nc};\ (\text{I}_{nc})$$

$$\text{TPH} \rightarrow \text{Ph}_2\text{N}^\bullet \xrightarrow{+\text{PhSH}} \text{PhS}^\bullet,\quad k_i; \quad (i)$$

$$\text{QDI} + \text{PhSH} \rightarrow \text{HQDI}^\cdot + \text{PhS}^\bullet,\quad k_1; \quad (\text{I})$$
$$\text{HQDI}^\cdot + \text{PhSH} \rightarrow \text{H}_2\text{QDI} + \text{PhS}^\bullet,$$

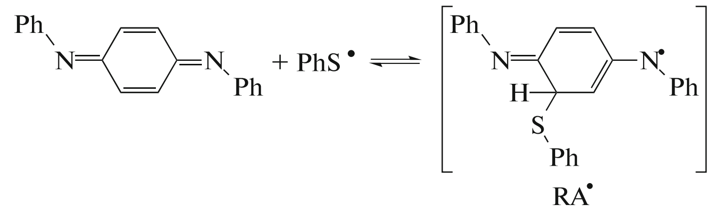
$$\text{PhS}^\bullet + \text{QDI} \leftrightarrow \text{RA}^\bullet \rightarrow \text{AmN}^\bullet\text{Ph},\quad k_2; \quad (\text{II})$$

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

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

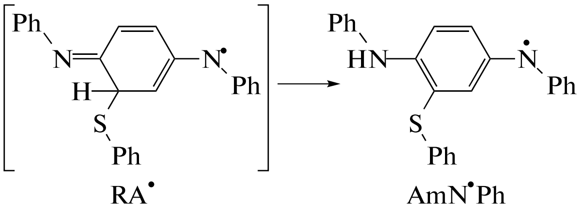
Tetraphenylhydrazine ($Ph_2N{-}NPh_2$, TPH) is specified here as the initiator, which decomposes upon heating to diphenylaminyl $Ph_2N^{\bullet}$ radicals that do not interact with QDI but are very active in the abstraction of mobile H atoms [25]. In Scheme 1, we assume the total reaction proceeds by two routes, one chain and one nonchain. Stage (I_{nc}) is a bimolecular reaction of nonchain interaction between the reagents, and the remaining stages belong to a chain reaction.

According to Scheme 1, the formation of 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 in the absence of an initiator proceeds according to bimolecular reaction (I) between QDI and PhSH. $HQDI^{\bullet}$ radicals are then replaced with $PhS^{\bullet}$ radicals, one of the two types of radicals that lead the chain of the total chain reaction, according to the reaction with PhSH. $PhS^{\bullet}$ radicals propagate the chain by participating in complex reaction (II), which includes the formation of an unstable $RA^{\bullet}$ radical adduct:

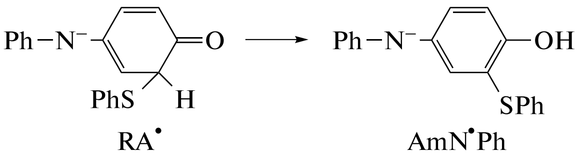


(a, f)

Reversible reaction (a, f) of the association and fragmentation of the $RA^{\bullet}$ adduct is introduced into the mechanism in analogy with the reversible reaction of adduct formation between thiyl radicals and unsaturated hydrocarbons known from the literature [26–29]. In the above mechanism (see Scheme 1), we assume that the $RA^{\bullet}$ radical adduct can not only defragment into the initial reagents but also isomerize to an $AmN^{\bullet}Ph$ thio-substituted diarylaminyl radical that acts as the second type of radicals which lead the chain at stage (III)

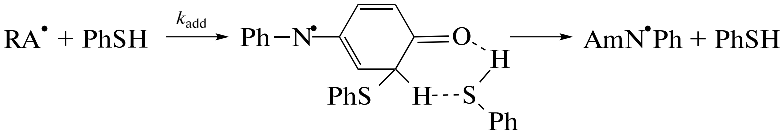


(iso)



(iso)

Reaction (iso) was specially considered by means of quantum chemistry in [30]. It was found that as a result of its high energy of activation, this reaction barely proceeds along the route of intramolecular transfer of the highly mobile H atom of the C–H bond of the ring to the nitrogen atoms of QDI (or to the O and N atoms in the case of the reaction of PhSH with *N*-phenyl-1,4-benzoquinone monoimine ($C_6H_5{-}N{=}C_6H_4{=}O$, QMI)). For example, the energy of activation of the monomolecular isomerization of the adduct formed when a $PhS^{\bullet}$ radical “adheres” to QMI is ~200 kJ/mol, which even exceeds the strength of the C–H bond that breaks as the reaction proceeds (~160 kJ/mol) [30]. For reaction (iso), an alternative bimolecular mechanism was proposed that included embedding a thiol into a four-membered transition state, thereby expanding it to a six-membered transition state favoring the reaction. When the reaction is complete, the thiol regenerates; i.e., it acts as a catalyst for the chain reaction at complex stage (II) of chain propagation:



(iso_{cat})

Experimental data testify to reaction (II) being the limiting stage of chain propagation [16, 17]. The form of the expression for the rate of this stage (i.e., rate w_{AmNPh} of the formation of $AmN^{\bullet}Ph$) depends on the ratio of the rate constants of the reactions of association k_{a}, fragmentation k_{f}, and isomerization k_{add} of radical adduct RA$^\bullet$. If $k_{\text{add}}[\text{PhSH}] \gg k_{\text{f}}$, then

$$\begin{gathered} w_2 = k_2[\text{QDI}][\text{PhS}^\bullet] = w_{\text{AmNPh}} \\ = k_{\text{add}}[\text{PhSH}][\text{RA}^\bullet] = k_{\text{a}}[\text{QDI}][\text{PhS}^\bullet], \\ k_2 = k_{\text{a}}. \end{gathered} \tag{3a}$$

If $k_{\text{f}} \gg k_{\text{add}}[\text{PhSH}]$, then $\text{RA}^\bullet = (k_{\text{a}}/k_{\text{f}})[\text{QDI}][\text{Ph S}^\bullet]$, so

$$\begin{gathered} w_2 = k_2[\text{QDI}][\text{PhS}^\bullet] = w_{\text{AmNPh}} \\ = k_{\text{add}}[\text{PhSH}][\text{RA}^\bullet] \\ = (k_{\text{add}}k_{\text{a}}/k_{\text{f}})[\text{PhSH}][\text{QDI}][\text{PhS}^\bullet], \\ k_2 = (k_{\text{add}}k_{\text{a}}/k_{\text{f}})[\text{PhSH}]. \end{gathered} \tag{3b}$$

The experiment shows that the main parameter of the chain reaction between QDI and PhSH $k_2/k_4^{1/2}$ (see below) does not depend on the concentration of PhSH [17–19]. This indicates that when the reaction occurs, correlation (3a) is observed; i.e., inequality $k_{\text{add}}[\text{PhSH}] \gg k_{\text{f}}$ holds at the lowest experimental concentrations of PhSH. We would therefore expect that the value of k_2, determined by the kinetic patterns of the chain reaction between QDI and PhSH is the same as that of k_{a}, i.e., the rate constant of the PhS$^\bullet$ radical "sticking" to the double C=C bond of the cyclohexadiene ring of quinone diimine QDI. Let us estimate k_2 from the values of $k_2/k_4^{1/2}$ in Table 1. Assuming that the rate constant of the recombination of the PhS$^\bullet$ phenylthiyl radicals is close to diffusion limit $k_4 = 6 \times 10^9$ L mol^{-1} s^{-1} [31, 32], we obtain $k_2 = 1.2 \times 10^6$ L mol^{-1} s^{-1} in chlorobenzene. This estimate falls in the range of experimentally measured rate constants of the reactions of PhS$^\bullet$ addtion to olefins of different structures in various solvents [32]. By assuming that k_4 does not depend on the concentration of propanol-1,[1] we obtained the values of k_2 in chlorobenzene + propanol-1 mixed solvents that are presented in Table 1. It is seen that the value of k_2 is halved when the solvent changes from chlorobenzene to propanol-1.

Let us discuss the possible reasons for the drop in k_2. In principle, we can expect dual action of propanol-1 on k_2. Propanol-1 can evidently accelerate the isomerization of the RA$^\bullet$ radical adduct to the AmN$^\bullet$Ph radical catalytically, similar to that of thiophenol (PhSH) considered above [30]. However, no notable effect of propanol-1 on the reaction rate should be expected, despite the much higher concentration of the alcohol, relative to PhSH. It follows from the above that PhSH efficiently catalyzes the isomerization of RA$^\bullet$ to AmN$^\bullet$Ph even at the lowest experimental concentrations; i.e., inequality $k_{\text{add}}[\text{PhSH}] \gg k_{\text{f}}$ holds.

The opposite inhibitory action of propanol-1 on stage (II) can be expected as a result of the complex formation of quinone imine with propanol-1. Quinone imines form complexes with both chlorobenzene and propanol-1, and the complexes with propanol-1 are much stronger [34]. Complex formation is mainly due to the formation of H complexes; in quinone imines, both their heteroatoms (N atoms in QDI, along with N and O atoms in QMI) and π electron systems act as proton acceptors. Enthalpies of formation ΔH of hydrogen-bound complexes of quinone imines with propanol-1, in which the heteroatoms of quinone imines are proton acceptors, were determined in [34] by means of quantum chemistry and the additive–multiplicative model of hydrogen bonds [35]. Values that were quite high and close to each other were obtained for both quinone imines: $\Delta H = -23$ kJ mol^{-1}.

When discussing the effect of propanol-1 on k_2, the thermodynamic characteristics of the H-complexes formed during the interaction between the protons of alcohol and π-electron systems of quinone imines, the reaction centers of the reaction, are of much greater interest. These data were not presented in [34], so we calculated enthalpy of formation ΔH of such complexes in this work using the additive–multiplicative model for this as well [35]. This model allowed us to calculate the enthalpy of H complex formation of two particles with one hydrogen bridge under the standard conditions (1) a composition of the complex of 1 : 1; (2) a temperature of 298 K; and (3) CCl$_4$ as the solvent. We calculate ΔH using the formula

$$\Delta H,\ \text{kJ mol}^{-1} = 4.96 E_{\text{a}} E_{\text{d}},$$

where E_{a} and E_{d} are empirical enthalpic proton-accepting (for the π system of quinone imines) and proton-donating (propanol-1) factors that characterize the relative capability of compounds to form hydrogen bonds. We found the values of E_{a} and E_{d} using the HYBOT program [36]:

$$\begin{gathered} E_{\text{a}} = 0.38\ (\text{for the } \pi \text{ system of quinone imines}), \\ E_{\text{d}} = -1.54\ (\text{for the H atom of propanol-1}). \end{gathered}$$

Based on these values of E_{a} and E_{d}, we obtain

$$\Delta H(\pi\ldots\text{HO}) = -2.90\ \text{kJ mol}^{-1}.$$

As we can see, the reaction of formation of π complexes is weakly exothermic. Despite the estimated nature of the obtained value of ΔH, these data show this reaction can indeed make some contribution to the processes in the system. The formation of complexes with propanol-1 blocks the π systems of quinone imines; i.e., it lowers their effective concentra-

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[1] When studying reactions with the participation of thiyl radicals, their solvation by solvents (particularly alcohols) is generally not considered [28, 33].

tions, the reaction centers in reaction (2) of $PhS^{\bullet}$ radicals “sticking” to the cyclohexadiene rings of quinone imine. A consequence of the formation of π complex could be a drop in k_2 when the solvent is changed from chlorobenzene to propanol-1. The data in Table 1 agree with this conclusion.

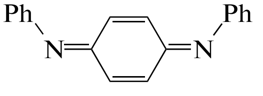
An alternative interpretation of the effect of propanol-1 on k_2 can also be obtained with the electrostatic models of nonspecific solvation. Using the data in Table 1, we built the dependence of lg k_2 on the Kirkwood function (ε − 1)/(2ε + 1) (see Fig. 1):

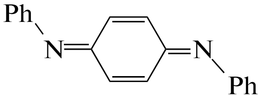
$$\log k_2 = \log k_{2(0)} - \frac{1}{2.303kT}\frac{\varepsilon - 1}{2\varepsilon + 1}\left(\frac{\mu^2_{PhS^{\bullet}}}{r^3_{PhS^{\bullet}}} + \frac{\mu^2_{QDI}}{r^3_{QDI}} - \frac{\mu^2_{\neq}}{r^3_{\neq}}\right), \quad (4)$$

where μ and r are the dipole moments and radii of reagents $PhS^{\bullet}$ and QDI, along with the activated complex of reaction (2) between $PhS^{\bullet}$ and QDI. It is seen that the experimental points satisfactorily fall on a straight line:

$$\log k_2 = (7.2 \pm 0.2) - (3.0 \pm 0.4)(\varepsilon - 1)/(2\varepsilon + 1),$$
$$R = 0.969.$$

As might be expected, this line has a gentle slope, as is characteristic of radical reactions. The negative value of the slope testifies to the activated complex being less polar than the total polarity of the reagents. It is, however, difficult to obtain additional information, due largely to quinone diimine (QDI) existing in two of its forms: *syn*- and *anti*-, which differ strongly with respect to their properties (in the gas phase, μ_{syn} = 2.11 D and μ_{anti} = 0 D [30]). In solutions, both forms are present in comparable concentrations but their absolute values are unknown


syn-QDI


anti-QDI

Let us discuss the effect the solvent has on the rates of the reaction by each route and the composition of the products. The following expression for the total rate w_{QDI} of the reaction is obtained from kinetic scheme of the reaction:

$$w_{QDI} = (k_1 + k_{nc})[QDI][PhSH] + \frac{k_2}{k_4^{1/2}}[QDI]\{0.5w_i + k_1[QDI][PhSH]\}^{1/2}, \quad (5)$$

where w_i is the rate of initiation upon the decomposition of the initiator. Expression (5) considers the consumption of QDI in the chain reaction, by the nonchain channel (I_{nc}), and in stage (I) of radical formation (we must consider the rate of this stage for short chains).

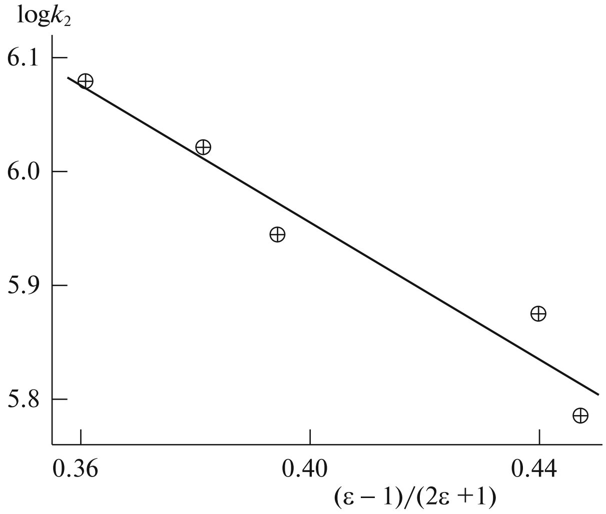


Fig. 1. Dependence of log k_2 on function (ε − 1)/(2ε + 1) of binary solvent chlorobenzene + propanol-1 at 343 K.

Table 1 presents the average values of k_1 and k_{1nc} obtained in [19] from processing the results from experiments with and without the initiator, according to Eq. (5). Table 1 shows that upon moving from chlorobenzene to propanol-1, the values of k_1 and k_{1nc} grow to almost the same extent (by approximately 20 times), and the absolute values of k_1 are 20–30 times lower than those of k_{1nc}, regardless of the composition of the mixed solvent.

Using the rate constants of the reactions from Table 1, we calculated rates w_{QDI} of the total reaction and both its routes (nonchain w_{nc} and chain w_c) at several concentrations of reagents $[QDI]_0$ and $[PhSH]_0$ from the range of variation of their values in actual experiments. Our results are presented in Table 2. For comparison, Table 2 also presents the experimental data for the experiments at $[QDI]_0 = 8.6 \times 10^{-5}$ and $[PhSH]_0 = 2.75 \times 10^{-3}$ mol L^{-1}.

It is seen from Table 2 that the rates of both routes of the reactions grow along with N_{PrOH}, and the rate of the nonchain route w_{nc} grows faster than that of chain route w_c. This is also indicated by the results from calculating the ratio of the rate of the chain route to the rate of total reaction w_c/w_{QDI} (see Table 2). One consequence of the drop in the w_c/w_{QDI} ratio with the growth in N_{PrOH} is apparently an increase in the yield of the products of the nonchain reaction when the solvent is changed from chlorobenzene to propanol-1. In addition, it follows from the data of Table 2 that replacing the solvent is accompanied by a reduction in chain length ν of the chain reaction. This means that when chlorobenzene is replaced with propanol-1, an increase is observed in the yield of the products formed at the stages of chain initiation and termination (i.e., H_2QDI and PhSSPh). This agrees with the

Table 2. Kinetic parameters of the reaction between QDI and PhSH, depending on the molar fraction of propanol-1 N_{PrOH} in PhCl + PrOH binary solvents and the experimental reaction rates (the values in brackets) at $[\mathrm{QDI}]_0 = 8.6 \times 10^{-5}$ and $[\mathrm{PhSH}]_0 = 2.75 \times 10^{-3}$ mol L^{-1} [19] ($T = 343 \pm 0.2$ K; argon bubbling)

$[\mathrm{QDI}] \times 10^4$	$[\mathrm{PhSH}] \times 10^4$	$w_{\mathrm{i(0)}} \times 10^9$	$w_{\mathrm{QDI}} \times 10^8$	$w_{\mathrm{nc}} \times 10^8$	$w_{\mathrm{c}} \times 10^8$	$w_{\mathrm{c}}/w_{\mathrm{QDI}}$	Chain length
mol L^{-1}		mol L^{-1} s^{-1}					
$N_{\mathrm{PrOH}} = 0$							
1	1	0.168	1.66	0.252	1.41	0.848	83.3
3	1	0.504	8.05	0.756	7.30	0.906	144.3
1	5	0.84	4.43	1.26	3.17	0.716	37.3
3	5	2.52	20.2	3.78	16.4	0.813	64.5
0.86	27.5	3.97	12.0	5.96	6.05	0.504	14.7
0.86	27.5		(13.7)				
$N_{\mathrm{PrOH}} = 0.194$							
1	1	0.828	3.30	0.96	2.34	0.709	27.8
3	1	2.48	15.0	2.88	12.1	0.808	48.2
1	5	4.14	10.2	4.80	5.35	0.527	12.4
3	5	12.4	41.8	14.4	27.4	0.655	21.5
0.86	27.5	19.6	33.3	22.7	10.6	0.318	4.9
0.86	27.5		(23.7)				
$N_{\mathrm{PrOH}} = 0.803$							
1	1	3.93	7.70	3.20	4.50	0.585	11.0
3	1	11.8	32.6	9.6	23.0	0.705	19.0
1	5	19.7	26.6	16.0	10.6	0.399	4.9
3	5	58.9	101.0	48.0	53.0	0.525	8.5
0.86	27.5	92.9	98.3	75.7	22.7	0.230	1.9
0.86	27.5		(124.5)				
$N_{\mathrm{PrOH}} = 1$							
1	1	3.93	8.51	4.8	3.71	0.436	8.9
3	1	11.8	33.2	14.4	18.8	0.567	15.5
1	5	19.6	32.8	24.0	8.83	0.269	4.0
3	5	58.9	115.7	72.0	43.7	0.378	6.9
0.86	27.5	92.8	132.8	113.5	19.3	0.145	1.6
0.86	27.5		(180.9)				

$w_{\mathrm{i(0)}} = 2k_1[\mathrm{QDI}][\mathrm{PhSH}]$, $w_{\mathrm{nc}} = k_{1\mathrm{nc}}[\mathrm{QDI}][\mathrm{PhSH}]$, $w_{\mathrm{c}} = w_{\mathrm{QDI}} - w_{\mathrm{nc}}$, chain length $\nu = (w_{\mathrm{c}}/w_{\mathrm{i(0)}}) - 0.5$.

scarce literature data, which were, however, obtained at relatively great depths of conversion. The considerable effect the nature of the solvent has on the composition of the products of the reaction of QMI with thiols was thus observed in [12].

The data in Tables 2 and 1 apparently do not contradict one another. Indeed, when N_{PrOH} is increased, the values of k_1 and $k_{1\mathrm{nc}}$ in Table 1 grow in proportion to one another. At the same time, it follows from Table 2 that the rate of the nonchain route w_{nc} in this case grows faster than that of chain route w_{c}. In fact, this "contradiction" is explained by a decrease in the chain length ν of the chain reaction with an increase in N_{PrOH} (see the last column of Table 2).

Let us consider the expression for chain length ν in more detail. For this we obtain the expression for the rate of chain reaction $w_{\mathrm{c}} = w_{\mathrm{QDI}} - w_{\mathrm{nc}} = w_{\mathrm{QDI}} - k_{1\mathrm{nc}}[\mathrm{QDI}][\mathrm{PhSH}]$ from Eq. (5) and divide it by the rate of chain initiation in non-initiated reaction $w_{\mathrm{i(0)}} = 2k_1[\mathrm{QDI}][\mathrm{PhSH}]$:

$$\nu = \frac{w_{\mathrm{c}}}{w_{\mathrm{i(0)}}} = \frac{w_{\mathrm{QDI}} - w_{\mathrm{nc}}}{2k_1[\mathrm{QDI}][\mathrm{PhSH}]} = 0.5 + \frac{k_2}{2k_4^{1/2}k_1^{1/2}}\left(\frac{[\mathrm{QDI}]}{[\mathrm{PhSH}]}\right)^{1/2}. \tag{6}$$

The first summand 0.5 in the right part of (5) considers the consumption of QDI in reaction (I) of radical formation, and this summand can be ignored for fairly long chains.

It is seen from (6) that the second member in the right part depends on cofactor $k_2/2(k_4k_1)^{1/2}$ at the same ratio of the concentrations of QDI and PhSH. Table 1 shows that upon moving from chlorobenzene to propanol-1, parameter $k_2/(2k_4)^{1/2}$ is only halved. This is insufficient for explaining the fairly large drop in chain length upon an increase in N_{PrOH}. The growth in k_1 (i.e., the almost twentyfold increase in the rate of initiation upon a rise in N_{PrOH} when moving from chlorobenzene to propanol-1; see Table 1) thus has a stronger effect on v, since chain length is inversely proportional to $k_1^{1/2}$.

Based on the data in Table 2, we may conclude that the composition of the products at the initial stages of the reaction depends not only on the nature of the solvent but on the ratio of the concentrations of the initial reagents as well. To determine the effect the concentrations of QDI and PhSH have on the composition of the products, we obtain the expression for w_c/w_{QDI} from (5). For simplicity, we ignore k_1 relative to k_{nc} in the first summand in the right part of (5) and obtain the following for the noninitiated reaction ($w_i = 0$):

$$\frac{w_c}{w_{\text{QDI}}} = \left[1 + \frac{k_{1\text{nc}}k_4^{1/2}}{k_1^{1/2}k_2}\left(\frac{[\text{PhSH}]}{[\text{QDI}]}\right)^{1/2}\right]^{-1}. \qquad (7)$$

As is seen from (7), the yield of the products of the chain reaction grows along with the concentration of QDI and falls as the concentration of PhSH grows.

CONCLUSIONS

Our results show that the patterns of the bidirectional reaction between PhSH and QDI depend largely on the concentration of propanol-1 in mixtures of it and chlorobenzene. At 343 K, replacing chlorobenzene with propanol-1 increases the rate of the total reaction by more than an order of magnitude, and the rate of the nonchain route grows more than that of the chain route. With an increase in the concentration of propanol-1, the chain length of the chain reaction decreases, and this affects the composition of the products of the reaction between PhSH and QDI. Replacing chlorobenzene with propanol-1 halves the rate constant of the limiting stage of chain propagation (the reaction between quinone diimine and the phenylthiyl radical), which is satisfactorily explained by the formation of H complexes between the π system of quinone diimine and the proton of propanol-1.

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REFERENCES

1. P. J. O'Brien, Chem.-Biol. Interact. **80**, 1 (1991).
2. T. J. Monks, R. P. Hanzlik, G. M. Cohen, et al., Toxicol. Appl. Pharmacol. **112**, 2 (1992).
3. L. Wlodek, Pol. J. Pharmacol. **54**, 215 (2002).
4. Y. Kumagai, J. Health Sci. **55**, 887 (2009).
5. D. C. Dahlin, G. T. Miwa, A. Y. Lu, and S. D. Nelson, Proc. Nat. Acad. Sci. U. S. A. **81**, 1327 (1984).
6. S. D. Cohen and E. A. Khairallah, Drug. Metabol. Rev. **29**, 59 (1997).
7. W.-W. Li, J. Heinze, and W. Haehnel, J. Am. Chem. Soc. **127**, 6140 (2005).
8. J. M. Snell and A. Weissberger, J. Am. Chem. Soc. **61**, 450 (1939).
9. *The Chemistry of the Quinoid Compounds,* Ed. by S. Patai (Wiley, London, New York, Sydney, Toronto, 1974), Vol. 1, Ch. 1-2.
10. *The Chemistry of the Quinoid Compounds,* Ed. by S. Patai and Z. Ruppoport (Wiley, Chichester, New York, Toronto, Singapore, 1988), Vol. 2, Ch. 1-2.
11. A. A. Kutyrev and V. V. Moskva, Russ. Chem. Rev. **60**, 72 (1991).
12. G. B. Afanas'eva, E. V. Tsoi, O. N. Chupakhin, E. O. Sidorov, and S. V. Konovalov, Zh. Org. Khim. **21**, 1926 (1985).
13. M. K. Vadnere, L. Maggiora, and M. P. Mertes, J. Med. Chem. **29**, 1714 (1986).
14. S. Lu, W-W. Li, D. Rotem, E. Mikhailova, and H. Bayley, Nat. Chem. **2**, 921 (2010).
15. A. V. Gadomskaya and V. T. Varlamov, Dokl. Phys. Chem. **439**, 150 (2011).
16. A. V. Gadomska, S. Ya. Gadomsky, and V. T. Varlamov, Kinet. Catal. **53**, 525 (2012).
17. V. T. Varlamov and A. V. Gadomska, Russ. J. Phys. Chem. A **89**, 616 (2015). doi 10.7868/S0044453715040299
18. V. T. Varlamov, S. Ya. Gadomsky, and A. V. Gadomska, Kinet. Catal. **56**, 276 (2015). doi 10.1134/S0023158415030222
19. V. T. Varlamov and A. V. Gadomska, Russ. Chem. Bull. **65**, 2046 (2016). doi 10.1007/s11172-016-1550-5
20. N. Takahashi, J. Schreiber, V. Fisher, and R. P. Mason, Arch. Biochem. Biophys. **252**, 41 (1987).
21. J. Butler and B. M. Hoey, Free Rad. Biol. Med. **12**, 337 (1992).
22. Yu. Ya. Fialkov, *Solvent As Control Facility of Chemical Process* (Khimiya, Leningrad, 1990) [in Russian].
23. O. W. Maender, C. J. Rostek, A. R. Katritzky, H. H. Odens, and M. V. Voronkov, US Patent No. 7718722 (2010).
24. I. R. Gelling and G. T. Knight, in *Plastics and Rubber: Processing* (1977), p. 83.
25. E. T. Denisov and V. T. Varlamov, Kinet. Catal. **38**, 28 (1997).

26. C. Walling and W. Helmreich, J. Am. Chem. Soc. **81**, 1144 (1959).
27. K. Griesbaum, Angew. Chem., Int. Ed. Engl. **9**, 273 (1970).
28. Ch. Chatgilialoglu, A. Altieri, and H. Fischer, J. Am. Chem. Soc. **124**, 12816 (2002).
29. O. Türün and M. A. R. Meier, Eur. J. Lipid Sci. Technol. **115**, 41 (2013).
30. V. T. Varlamov and B. E. Krisyuk, Russ. Chem. Bull. **65**, 401 (2016). doi 10.1007/s11172-016-1312-4
31. O. Ito, K. Nogami, and M. Matsuda, J. Phys. Chem. **85**, 1365 (1981).
32. O. Ito, in *The Chemistry of Free Radicals. S-Centered Radicals,* Ed. by Z. B. Alfassi (Wiley, Chichester, New York, etc., 1999), Ch. 6.
33. C. Chatgilialoglu and K.-D. Asmus, *Sulfur-Centered Reactive Intermediates in Chemistry and Biology,* Vol. 197 of *NATO ASI Series A: Life and Science* (Plenum, New York, 1990), p. 327.
34. V. T. Varlamov, B. E. Krisyuk, and V. Yu. Grigor'ev, Russ. Chem. Bull. **67**, 1851 (2018). doi 10.1007/s11172-018-2298-x.
35. O. A. Raevsky, V. Yu. Grigor'ev, D. B. Kireev, and N. S. Zefirov, Quant. Struct.-Act. Relat. **11**, 49 (1992).
36. O. A. Raevskii, V. Yu. Grigor'ev, and S. V. Trepalin, Registration Certificate of Computer Program HYBOT (Hydrogen Bond Thermodynamics) No. 990090 (1999).

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