ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 5, pp. 525–530. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © A.V. Gadomska, S.Ya. Gadomsky, V.T. Varlamov, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 5, pp. 550–555.

Chain Mechanism of the Reactions of *N*,*N*'-Diphenyl-1,4-Benzoquinone Diimine with Thiophenol and 1-Decanethiol

A. V. Gadomska, S. Ya. Gadomsky, and V. T. Varlamov

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

Received October 21, 2011

Abstract—The kinetics of the reactions of *N*,*N*'-diphenyl-1,4-benzoquinone diimine with thiophenol and 1-decanethiol in chlorobenzene at 343 K has been investigated spectrophotometrically in an argon atmosphere with monitoring of the disappearance of quinone diimine as its absorbance in the visible range. The acceleration of the reactions in the presence of initiators—tetraphenylhydrazine and azobisisobutyronitrile—indicates that the reactions proceed via a chain mechanism under the chosen experimental conditions. The chain length of the reactions in the absence of an initiator is estimated: $\nu \approx 10$ units in the reaction of quinone diimine with thiophenol and $\nu \approx 100$ units in the reaction with 1-decanethiol at a quinone diimine concentration of about 10^{-4} mol/L and thiol concentrations of about 10^{-3} mol/L. The dependence of the kinetic parameters of the initiated reaction on the thiophenol concentration suggests that the reaction of the thiyl radical with quinone diimine is the rate-determining step of chain propagation. The rate constant of this reaction is estimated at $k_{\mathrm{pr}} = 3.2 \times 10^5$ L mol^{-1} s^{-1}. The rates of chain initiation due to the direct interaction of the initial reactants are estimated. In these reactions, the homolytic cleavage of the S–H bond occurs in the thiol, due to which, other conditions being equal, the radical formation rate in the quinone diimine–thiophenol system is at least two orders of magnitude higher than that in the quinone diimine–1-decanethiol, in which the strength of S–H bond is higher. A radical chain mechanism is proposed for the reaction of quinone diimine with the thiols on the basis of the data obtained.

DOI: 10.1134/S0023158412050072

It has recently been established that the reaction of 2-mercaptobenzothiazole with 1,4-benzoquinone diimine in chlorobenzene occurs via a radical chain mechanism [1, 2]. This contradicts the common views concerning the mechanism of the reactions of thiols with quinone compounds, according to which these reactions proceed via the nucleophilic 1,4-addition of thiol to quinone (quinone imine) [3–7]. This mechanism is considered to occur in both polar solvents (with which most studies were carried out) and nonpolar media [8, 9]. The conclusions about the reaction mechanism are mainly based on the data on the composition of the stable final products, whereas kinetic data for the reactions of thiols with quinone compounds are lacking and are rather superficial [10].

The reactions of thiols with quinones are important for chemistry (they occur, for example, in technical rubbers oxidized in air and stabilized by secondary aromatic amines antioxidants [9]) and also for biochemistry and medicine. The latter is due to the fact that these reactions are one of the main cause of the high toxicity of quinoid compounds (from the environment or drugs and/or their metabolites) [11–14].

Taking this into account, in this work we continued to study the regularities of the reactions of thiols with quinoid compounds. The first results obtained by the study of the kinetics of the reactions of *N*,*N*'-diphenyl-1,4-benzoquinone diimine C_6H_5–N=C_6H_4=N–C_6H_5 (QDI) with thiophenol (PhSH) and 1-decanethiol $C_{10}H_{21}SH$ (RSH) are presented below.

EXPERIMENTAL

The procedure of the synthesis and purification of QDI and initiator tetraphenylhydrazine (TPH) were described [15]. Thiophenol PhSH (Aldrich) and 1-decanethiol RSH (Aldrich) were used without additional purification. The solvent was chlorobenzene (Aldrich) purified according to a known procedure [15].

Azobisisobutyronitrile (AIBN) (Fluka) was purified as follows. A nearly saturated AIBN solution (~15 g) in benzene was passed through a column (diameter of 2 cm, length of 10 cm) with silica gel SiO_2-L (size fraction of 40–100 μ). The eluate was evaporated at ambient temperature until the volume of the mother liquor above the crystals was 10–15 mL. Thereafter, the crystals were filtered on a Buchner funnel and washed with small portions of cooled benzene. After vacuum drying, AIBN was rapidly recrystallized from a small amount of methanol. The precipitated crystals were washed on a filter with cold methanol and were dried in vacuo.

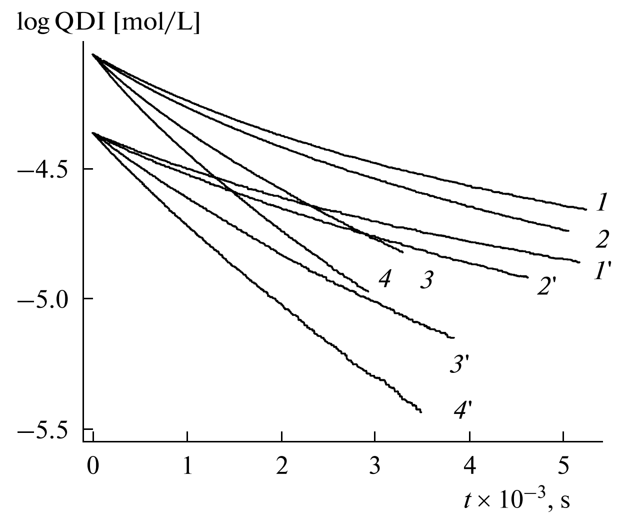


Fig. 1. Semilogarithmic anamorphoses of the of QDI disappearance curves in the chain reaction between QDI and PhSH. Initial concentrations: $[QDI]_0$ = (*1–4*) 8.60 × 10^{-5} and (*1'–4'*) 4.30 × 10^{-5} mol/L; $[PhSH]_0$ = 6.88 × 10^{-4} mol/L. TPH initiator; $w_{i(I)} \times 10^{-9}$ = (*1*, *1'*) 0, (*2*, *2'*) 0.76, (*3*, *3'*) 3.8, and (*4*, *4'*) 7.6 mol L^{-1} s^{-1}. Chlorobenzene, 343 K, Ar bubbling.

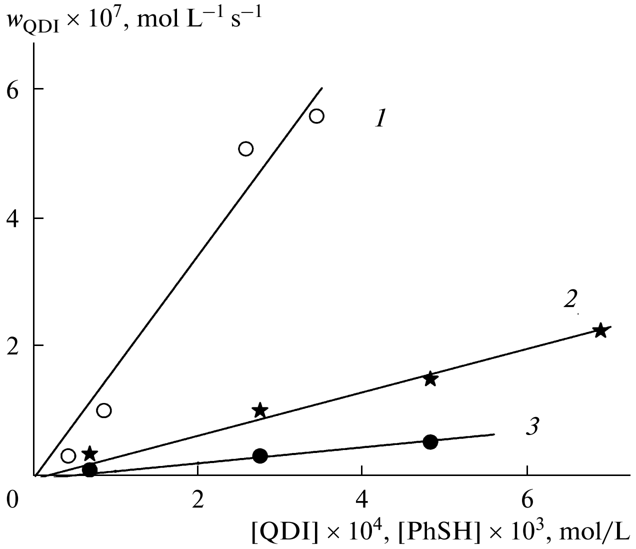


Fig. 2. Determination of the reaction orders from the dependence of the initial rate constant w_{QDI} on the concentration of one of the components at a constant concentration of another component: (*1*) initial rate as a function of $[QDI]_0$ at $[PhSH]_0$ = 2.75 × 10^{-3} mol/L, (*2*) initial rate as a function of $[PhSH]_0$ at $[QDI]_0$ = 8.60 × 10^{-5} mol/L, and (*3*) initial rate as a function of $[PhSH]_0$ at $[QDI]_0$ = 4.30 × 10^{-5} mol/L.

The reaction kinetics was studied by kinetic spectrophotometry. Experiments were carried out at 343 ± 0.2 K under argon in a bubbler-type reactor cell (volume of 6.5 mL, optical path of 2.0 cm) built in a Specord UV–VIS spectrophotometer. The reaction was monitored as the disappearance of QDI by measuring, at 1-s or shorter intervals, and displaying the absorbance of the solution at the absorption bands of QDI at 22260 cm^{-1} (ε = 6730 L mol^{-1} cm^{-1}), 20000 cm^{-1} (ε = 3755 L mol^{-1} cm^{-1}), or 19000 cm^{-1} (ε = 1690 L mol^{-1} cm^{-1}) [15], depending on the initial QDI concentration.

The following initiation rate constants at 343 K were used for initiators TPH and AIBN: k_i(TPH) = 1.96 × 10^{-4} s^{-1} [16] and k_i(AIBN) = 4.51 × 10^{-5} s^{-1} [17].

RESULTS AND DISCUSSION

The reaction of QDI with PhSH occurs rather rapidly even at low concentrations of the reactants (Fig. 1). The initial QDI disappearance rates (w_{QDI}) were used in the kinetic study, which were determined by fitting the QDI disappearance curves to the empirical equation

$$[QDI] = ae^{-bt} + c - dt \qquad (1)$$

or

$$[QDI] = a_1e^{-b_1t} + a_2e^{-b_2t}, \qquad (2)$$

where a–d, as well as a_1, a_2, b_1, and b_2, are constants fitted by the iteration methods. In most cases, Eq. (2) provides a good fit to the entire experimental kinetic curves. In some cases of using Eq. (1), fairly large segments of the curves for the late stages of the reaction should be excluded. The values of w_{QDI} determined by Eqs. (1) and (2) almost coincided.

According to Eqs. (1) and (2), w_{QDI} was calculated by the equation

$$w_{QDI} = ab + d \qquad (1a)$$

or

$$w_{QDI} = a_1b_1 + a_2b_2. \qquad (2a)$$

The dependences of w_{QDI} on the concentration of each reactant at a constant concentration of another reactant (Fig. 2) indicate that the initial rate of the reaction of QDI with PhSH depends linearly on the concentrations of QDI and PhSH ($n_{QDI} = 1$ and $n_{PhSH} = 1$); i.e.,

$$w_{QDI} \approx k_{eff}^{II}[QDI][PhSH], \qquad (3)$$

where k_{eff}^{II} is the effective second-order rate constant. However, the numerical values of k_{eff}^{II} determined from the slopes of the straight lines in Fig. 2 differ, being 0.63 ± 0.11 L mol^{-1} s^{-1} for line *1*, 0.39 ± 0.03 L mol^{-1} s^{-1} for line *2*, and 0.29 ± 0.02 L mol^{-1} s^{-1} for line *3*, which likely indicates a more complicated mechanism of the reaction.

In the presence of initiator I, the reaction rate increases (Figs. 1, 3), indicating that the reaction proceeds via the chain mechanism. The nature of the initiator exerts no effect on the kinetics of the initiated reaction (Fig. 3). The experimental dependences are satisfactorily linearized in the w_{QDI}^2–$w_{i(I)}$ coordinates (Fig. 3), where $w_{i(I)}$ is the rate of initiation due to the decomposition of initiator I. These results indicate that the chain termination follows a quadratic-law mechanism; that is,

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

and

$$w_{\mathrm{QDI}}^2 = A^2 w_{\mathrm{i}0} + A^2 w_{\mathrm{i(I)}}, \tag{4}$$

where $w_{\mathrm{i}0}$ is the rate of chain initiation in the system and the parameter A is

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

In Eq. (5), k_{pr} is the rate constant of the rate-determining step of chain propagation involving one of the chain carrier radicals and one of the starting compounds Sub (QDI or PhSH) and k_{t} is the rate constant of chain termination on these radicals.

The values of $w_{\mathrm{i}0}$ and A were calculated from the experimental data presented in Fig. 3 using Eq. (4). This made it possible to calculate the chain length for two concentrations of QDI and the parameter $k_{\mathrm{pr}}/(2k_{\mathrm{t}})^{0.5}$ (table), which is almost independent of $[\mathrm{QDI}]_0$. A twofold increase in the QDI concentration at the constant concentration $[\mathrm{PhSH}]_0 = 6.88 \times 10^{-4}$ mol/L results in an approximately twofold increase in the chain length and parameter A. We believe that this indicates that the rate-determining step of chain termination in the reaction of QDI with PhSH is the attack of thiyl radical $\mathrm{PhS}^{\bullet}$ on the double bond of the central cyclohexadiene moiety of quinone diimine; i.e., Sub = QDI in Eq. (5). The recombination of $\mathrm{PhS}^{\bullet}$ radicals should be considered as the chain termination step.

Using the recombination rate constant of radicals $\mathrm{PhS}^{\bullet}$ known from the literature ($2k_{\mathrm{t}} \approx 10^9$ L mol^{-1} s^{-1} [18]), we have $k_{\mathrm{pr}} \approx 3 \times 10^5$ L mol^{-1} s^{-1}, which agrees with published data [18, 19] for the rate constants of addition of the thiyl radicals to the double bond.

The kinetic regularities of the reaction change on passing from thiophenol to 1-decanethiol (Fig. 4). In the absence of an initiator, the kinetics of the reaction of QDI with RSH is characterized by self-acceleration periods, whose duration at [QDI] = const increases disproportionately strongly with an increasing RSH concentration (curves *1*, *1'*). The cause of the induction periods remains unclear. In particular, they cannot be explained by the prolonged establishment of the steady-state concentrations of radicals, which is characteristic of some chain reactions involving QDI, for example, the chain reaction of QDI with 2,5-dichlorohydroquinone [20]. Indeed, if the average lifetime of the chain in the steady state, $t = (2k_{\mathrm{t}} \times w_{\mathrm{i}0})^{-0.5}$, is used as the estimate of the duration of the induction period τ, we have that an increase in the RSH concentration in a series of experiments at [QDI] = const should shorten τ due to the increase in $w_{\mathrm{i}0}$, which contradicts the data of Fig. 4. The unsteady-state periods did not allow us to study the kinetics of the noninitiated reaction of QDI with RSH and, in particular, to determine the reaction orders with respect to the components.

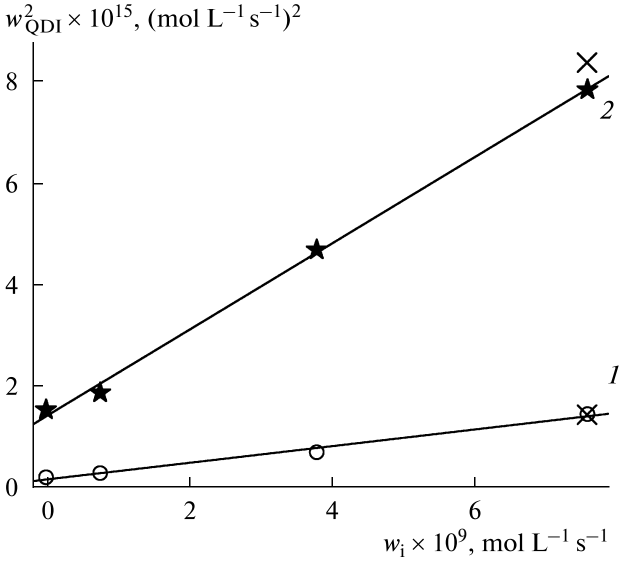


Fig. 3. Dependences of the squared rate of the reaction of QDI with PhSH (w_{QDI}^2) on the initiation rate ($w_{\mathrm{i(I)}}$). TPH initiator; $[\mathrm{PhSH}]_0 = \mathrm{const} = 6.88 \times 10^{-4}$ mol/L; $[\mathrm{QDI}]_0 =$ (*1*) 4.3×10^{-5} and (*2*) 8.6×10^{-5} mol/L. The experimental data obtained with the AIBN initiator are labeled with a cross. Chlorobenzene, 343 K.

As can be seen from Figs. 4 and 5, the initiator accelerates the reaction of QDI with RSH more strongly than it accelerates the reaction of QDI with PhSH. In the case of the reaction of QDI with RSH, the nature of the initiator exerts no effect on the kinet-

Kinetic parameters of the reactions of QDI with PhSH and RSH in chlorobenzene at 343 K

System	Concentration of reactants $\times 10^4$, mol/L		$w_{\mathrm{i}0} \times 10^9$, mol L^{-1} s^{-1}	$A \times 10^4$, (mol L^{-1} s^{-1})$^{0.5}$	ν	$k_{\mathrm{pr}}/(2k_{\mathrm{t}})^{0.5}$, (L mol^{-1} s^{-1})$^{0.5}$
	PhSH, RSH	QDI				
QDI–PhSH	6.88	0.43	1.1 ± 0.4	4.0 ± 0.1	12 ± 2	9.3 ± 0.3
	6.88	0.86	1.7 ± 0.2	9.2 ± 0.2	22 ± 1	10.7 ± 0.2
QDI–RSH	48.2	0.86	0.14 ± 0.06	17.0 ± 1.0	140 ± 90	20.0 ± 1.0

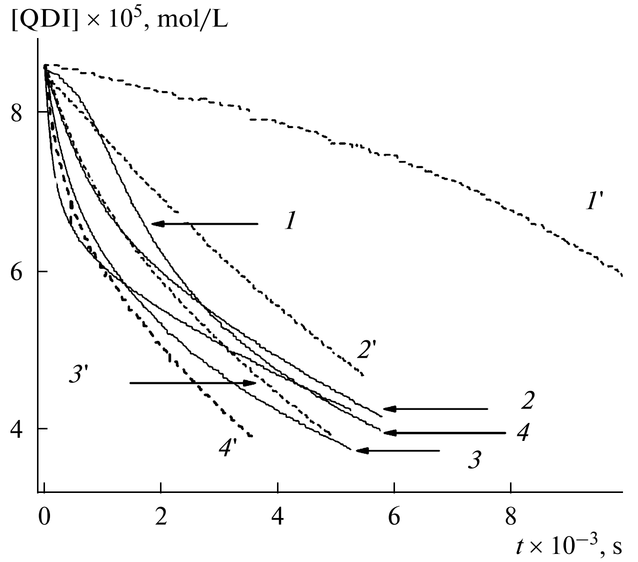
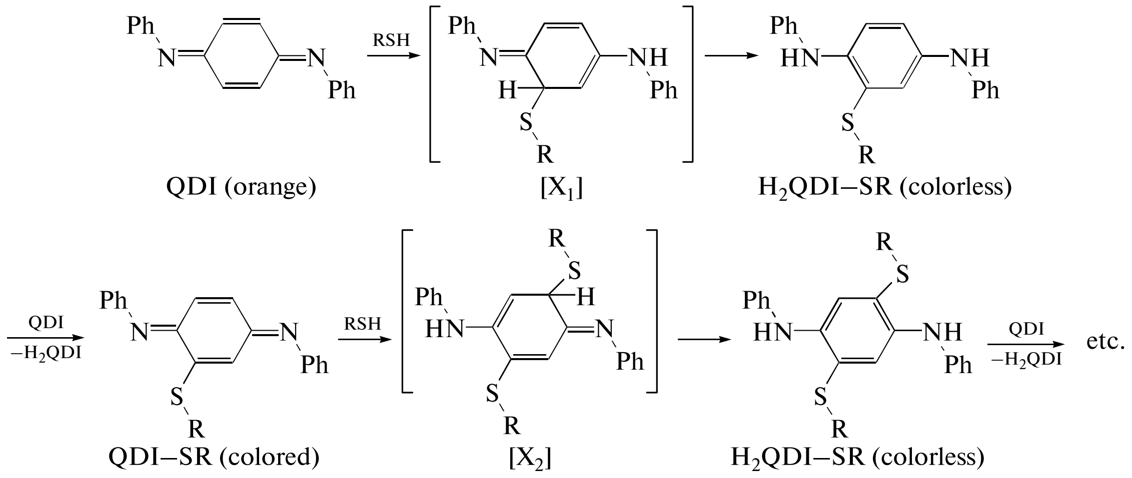


Fig. 4. QDI disappearance curves for the chain reaction between QDI and 1-decanethiol RSH. $[QDI]_0 = 8.60 \times 10^{-5}$ mol/L; $[RSH]_0$ = (*1–4*) 4.82×10^{-3} and (*1'–4'*) 8.95×10^{-3} mol/L. TPH initiator; $w_i \times 10^{-9}$ = (*1*, *1'*) 0, (*2*, *2'*) 0.76, (*3*, *3'*) 3.8, and (*4*, *4'*) 7.6 mol L^{-1} s^{-1}. Chlorobenzene, 343 K, Ar bubbling.

ics of the initiated reaction (Fig. 5). The experimental data are well linearized in the w^2_{QDI}–$w_{i(I)}$ coordinates (Fig. 5), and the straight lines pass almost through the point of origin, indicating a low chain initiation rate w_{i0}. The values of w_{i0} and A, the chain length, and the parameter $k_{pr}/(2k_t)^{0.5}$ for the reaction of QDI with RSH (table) were estimated from line *1* (table).

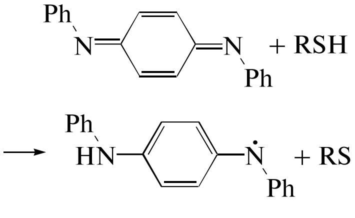
As can be seen, at the same concentration $[QDI]_0 = 8.6 \times 10^{-5}$ mol/L, the chain initiation rate w_{i0} in the QDI–PhSH system is almost one order of magnitude higher than that in the QDI–RSH system. Note that the RSH concentration is almost one order of magnitude higher than the concentration of PhSH. This fact unambiguously indicates that the S–H bond is cleaved at the radical formation stage. This correlates with the fact that the S–H bond strength is only ~330–340 kJ/mol, whereas for alkanethiols this value is substantially larger: ~370 kJ/mol [21, 22].

The results of the present work suggest a radical chain mechanism for the reactions of QDI with thiols. Since the composition of the products of similar reactions was reliably established and the reaction is known to be multistep, it should initially be specified what reaction or step of this mechanism is meant. As was mentioned above, it was found that the quinone compound is gradually enriched with thiyl residues during the reaction. According to the accepted mechanism, this occurs due to the nucleophilic 1,4-addition of thiols to the cyclohexadiene moiety of the starting compound and its partially substituted derivatives resulting from the reaction. This mechanism can be presented as the following sequence of reactions [3–5, 7, 8]:

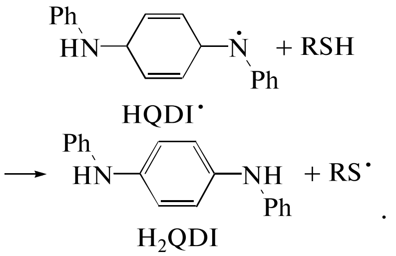


We believe that, when the thiol concentration considerably exceeds the concentration of quinone diimine ($[PhSH]_0$, $[RSH]_0 \gg [QDI]_0$), at the initial stages we can limit our consideration to the stage of formation of the first stable product, H_2QDI–SR.

The chain initiation stage includes the direct interaction of QDI with RSH yielding $RS^{\bullet}$ and $HQDI^{\bullet}$ radicals:



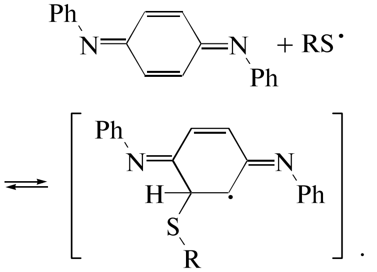
The $HQDI^{\bullet}$ radicals are rapidly replaced by radicals $RS^{\bullet}$by reacting with RSH:



Therefore, it can be assumed that only thiyl radicals are generated in the system at the chain initiation stage:

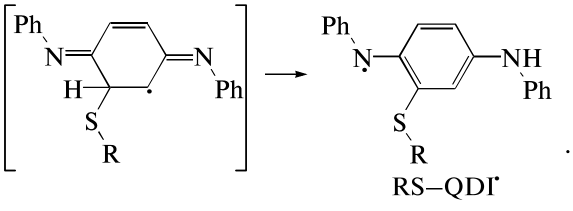
$$\mathrm{QDI} + 2\mathrm{RSH} \rightarrow \mathrm{H_2QDI} + 2\mathrm{RS}^{\bullet}. \qquad (\mathrm{I})$$

The $RS^{\bullet}$ radicals initiate the chain, entering into the reversible addition reaction at the double bond of the cyclohexadienyl moiety of the QDI molecule to form a carbon-centered radical:



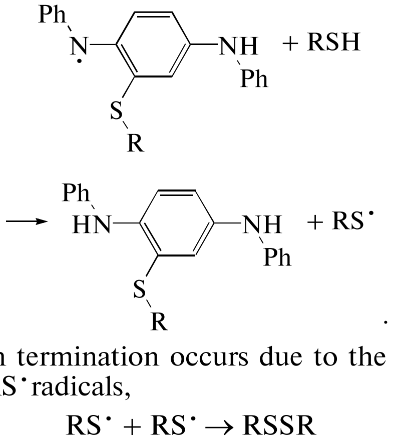
(II, –II)

As a result of the subsequent transformations, this radical is converted to the aminyl radical $RS–QDI^{\bullet}$, which is another chain carrier radical, in addition to $RS^{\bullet}$:



(IIa)

The reaction of H atom abstraction from the RSH molecule by the radical $RS–QDI^{\bullet}$ is the second step of chain termination:



(III)

Chain termination occurs due to the recombination of $RS^{\bullet}$ radicals,

$$\mathrm{RS}^{\bullet} + \mathrm{RS}^{\bullet} \rightarrow \mathrm{RSSR} \qquad (\mathrm{IV})$$

and, possibly, the disproportionation of $RS–QDI^{\bullet}$ radicals with $RS^{\bullet}$ radicals,

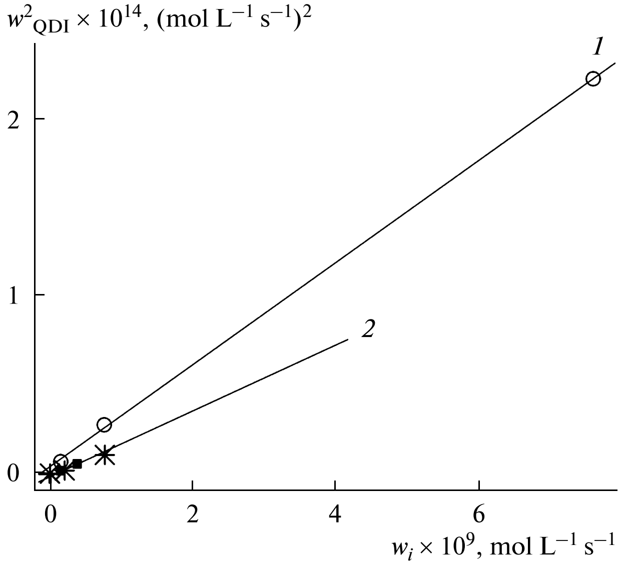
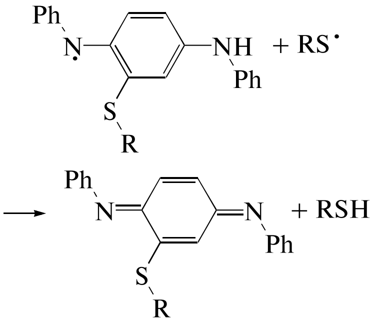
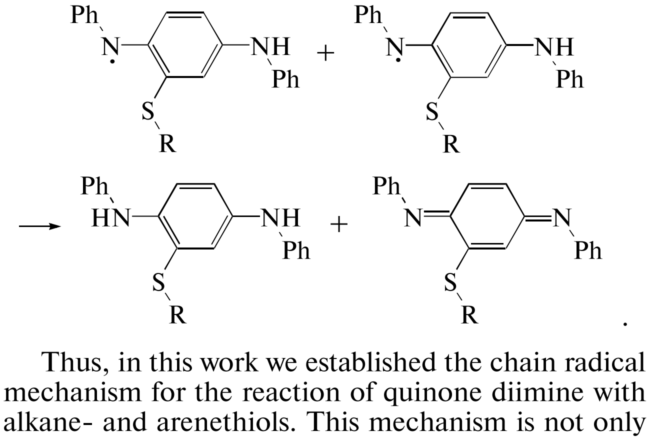


Fig. 5. Squared rate of QDI disappearance in the reaction between QDI and RSH (w^2_{QDI}) versus the initiation rate ($w_{i(I)}$). TPH initiator; $[QDI]_0 = 8.6 \times 10^{-5}$ mol/L; $[RSH]_0 =$ (*1*) 4.82×10^{-3} and (*2*) 8.95×10^{-3} mol/L. The experimental data obtained with the AIBN initiator ($[QDI]_0 = 8.6 \times 10^{-5}$ mol/L, $[RSH]_0 = 6.88 \times 10^{-3}$ mol/L) are labeled with a cross. Chlorobenzene, 343 K.



and/or with one another,



Thus, in this work we established the chain radical mechanism for the reaction of quinone diimine with alkane- and arenethiols. This mechanism is not only inherent in the earlier studied reaction of quinone diimine with 2-mercaprobenzothiazole [1, 2] but is also common for the reactions of quinone diimines with compounds containing the S–H group in the weakly polar solvent chlorobenzene.

ACKNOWLEDGMENTS

This work was supported by the Division of Chemistry and Materials Science of the Russian Academy of Sciences (program no. 1: "Theoretical and Experimental Study of the Chemical Bond Nature and Mechanisms of the Most Important Chemical Reactions and Processes").

REFERENCES

1. Gadomska, A.V. and Varlamov, V.T., *Butlerov Commun.*, 2010, vol. 23, no. 14, p. 62.
2. Gadomskaya, A.V. and Varlamov, V.T., *Dokl. Phys. Chem.*, 2011, vol. 439, part 2, p. 150.
3. Snell, J.M. and Weissberger, A., *J. Am. Chem. Soc.*, 1939, vol. 61, p. 450.
4. Porter, R.F., Rees, W.W., Frauenglass, E., Wilgus, H.S. III, Nawn, G.H., Chiesa, P.P., and Gates, J.R., Jr., *J. Org. Chem.*, 1964, vol. 29, p. 588.
5. Finley, K.T., in *The Chemistry of the Quinoid Compounds*, Patai, S., Ed., London: Wiley, 1974, part 2, ch. 17, p. 877.
6. Finley, K.T., in *The Chemistry of the Quinoid Compounds*, Patai, S. and Rappoport, Z, Eds., Chichester: Wiley, 1988, vol. 2, part 1, ch. 11, p. 537.
7. Kutyrev, A.A. and Moskva, V.V., *Usp. Khim.*, 1991, vol. 60, p. 134.
8. Afanas'eva, G.B., Tsoi, E.V., Chupakhin, O.N., Sidorov, E.O., and Konovalov, S.V., *Zh. Org. Khim.*, 1985, vol. 21, p. 1926.
9. Gelling, I.R. and Knight, G.T., *Plastic Rubber Process. Appl.*, 1977, vol. 2, p. 83.
10. Vadnere, M.K., Maggiora, L., and Mertes, M.P., *J. Med. Chem.*, 1986, vol. 29, p. 1714.
11. Cohen, C.D. and Khairallah, E.A., *Drug Metab. Rev.*, 1997, vol. 29, p. 59.
12. Li, W.-W., Heinze, J., and Haehnel, W., *J. Am. Chem. Soc.*, 2005, vol. 27, p. 6140.
13. Liebeke, M., Poether, D.-C., Duy, N., Albrecht, D., Becher, D., Hochgraefe, F., Lalk, M., Hecker, M., and Antelmann, H., *Mol. Microbiol.*, 2008, vol. 69, no. 6, p. 1513.
14. James, L.P., Mayeux, P.R., and Hinson, J.A., *Drug Metab. Dispos.*, 2003, vol. 31, no. 12, p. 1499.
15. Gadomsky, S.Ya. and Varlamov, V.T., *Russ. Chem. Bull.*, 2007, vol. 56, no. 12, p. 2376.
16. Varlamov, V.T., *Kinet. Catal.*, 2001, vol. 42, no. 6, p. 759.
17. Aleksandrov, A.L. and Krisanova, L.D., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, no. 11, p. 2469.
18. *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, New Series*, group II: *Atomic and Molecular Physics*, vol. 13: *Radical Reaction Rates in Liquids*, subvol. c: *Radicals Centered on N, S, P and Other Heteroatoms. Nitroxyls*, Hellwege, K.-H., Ed., Berlin: Springer, 1983, p. 308.
19. Chatgilialoglu, C., Altieri, A., and Fischer, H., *J. Am. Chem. Soc.*, 2002, vol. 124, p. 12816.
20. Gadomsky, S.Ya. and Varlamov, V.T., *Russ. J. Phys. Chem.*, 2009, vol. 83, p. 1704.
21. Denisov, E.T. and Tumanov, V.E., *Usp. Khim.*, 2005, vol. 74, p. 908.
22. Luo, Y.-R., *Handbook of Bond Dissociation Energies in Organic Compounds*, Boca Raton, Fla.: CRC, 2003.