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Molecular-Radical Catalysis of the Chain Reaction of Quinone Imine with Hydroquinone under the Action of Aromatic Amines

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Abstract—Secondary aromatic amines are catalysts of the chain reaction ($v = 10^3$ units) of *N*-phenyl-1,4-benzoquinone monoimine with 2,5-di-*tert*-butyl-1,4-hydroquinone. A complex mechanism of amine catalysis reveals that the rate of the chain reaction may increase, decrease, or remain unchanged in the presence of these compounds. In that case the product composition does not change, and amines are not consumed. The effects of temperature and the nature of *para* substituents (six species) on the activity of aromatic amines as catalysts were studied. A mechanism was proposed for the catalytic reaction; it implies the coupled occurrence of chain and catalytic processes. An expression for the rate of the catalytic reaction was obtained. The rate constants of individual steps with the participation of a catalyst and its radicals were calculated using the method of crossing parabolas. With the use of these data, a theoretical calculation of the dependence of the reaction rate on catalyst concentration was performed; the results were in good agreement with experimental data. The mechanism of the catalytic reaction was discussed; the similarities and distinctions between this mechanism and the mechanisms of other coupled chain reactions were demonstrated.

INTRODUCTION

The reaction of *N*-phenyl-1,4-benzoquinone monoimine (QMI, C_6H_5–N=C_6H_4=O) with 2,5-di-*tert*-butyl-1,4-hydroquinone (QH_2, 2,5[$(CH_3)_3C]_2C_6H_2(OH)_2$-1,4) occurs by a chain mechanism, and is characterized by very long chains of ~10^3 units [1]. Quinone imines are the nitrogen analogs of quinones; therefore, the above reaction belongs to a wider class of quinone reactions with hydroquinones. The mechanism of these reactions is of interest not only in chemistry but also in biology because it contributes to an understanding of the mechanism of the inhibiting action of quinone-type bioantioxidants (ubiquinones and vitamin K).

Previously [2], an unusual effect of aromatic amines on the above chain reaction was found with the use of 4,4'-dimethoxydiphenylamine as an example. It was found that at 340 K, depending on the concentrations of the reactants and the amine, the amine added either accelerated or inhibited the reaction, or the additive had no effect on the rate. In this case, no changes in the composition of products and no consumption of the amine were detected; hence, it followed that the amine acted as a catalyst in all instances. To explain the results, a mechanism was proposed; however, this mechanism was not reliably substantiated because the majority of elementary steps that constituted it were not characterized by experimental rate constants.

Presently, the rate constants of all the elementary steps of this mechanism can be calculated. This became possible because of the development of the parabolic model of a transition state (the method of crossing parabolas) [3] and the appearance of new experimental data on the kinetics of reactions with the participation of quinone monoimine. With consideration for the above, a kinetic study of the catalytic effects of a number of aromatic amines on the reaction of quinone imine with hydroquinone was performed. The results provided support for the mechanism of the catalytic reaction and elucidated its specific features.

EXPERIMENTAL

N-phenyl-1,4-benzoquinone monoimine (QMI) was prepared by the oxidation of 4-hydroxydiphenylamine ($QMIH_2$, C_6H_5–NH–C_6H_4–OH) with PbO_2. The synthesis was performed in a glass column packed with a mixture of PbO_2 with glass wool [4]. The primary purification of QMI was performed by recrystallization from methanol. 2,5-Di-*tert*-butyl-1,4-hydroquinone (QH_2), which was synthesized according to a published procedure [5], was kindly provided by I.K. Yakushchenko. The final purification of the reagents (QMI, QH_2, and aromatic amines) was performed by preparative liquid chromatography on SiO_2 (UV detector) with diethyl ether–hexane mixtures used as eluants (a mixture of ethyl acetate with benzene was used for QH_2). Chlorobenzene, which was purified as described elsewhere [4], was used as a solvent.

The experiments were performed in a thermostatted bubbling-type quartz reactor cell (volume of 8.5 cm^3; optical path length of 2.0 cm), which was placed in the cell compartment of a Specord UV–VIS spectrophotometer. The bubbling gas was argon; the temperatures

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were 298.2, 321.5, and 340.0 K (±0.5 K). In the course of experiments, the consumption of QMI was continuously monitored by measuring its absorption at λ = 450 nm, where the other reaction components practically did not absorb (as found in preliminary experiments). The molar absorption coefficient of QMI was determined with correction for the thermal expansion of chlorobenzene; the experimentally found values of ε are equal to 2995, 2950, and 2920 l mol^{-1} cm^{-1} at 298.2, 321.5, and 340.0 K, respectively.

Because the resulting products affect the kinetics of the reaction of QMI with QH_2 [1, 2], quantitative regularities were studied using the initial rates (w_{QMI}) of QMI consumption, when the effect of the products can be ignored. The values of w_{QMI} were obtained by the treatment of the kinetic curves of QMI consumption using the equation

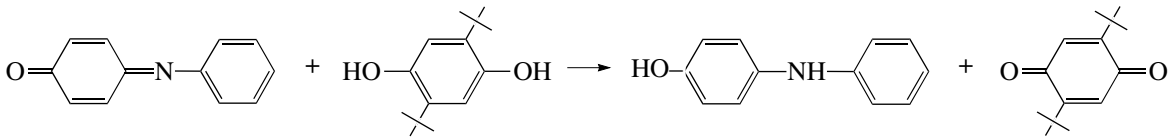
$$\ln(a + \ln[QMI]) = b + ct,$$

where a, b, and c are adjustable empirical constants. In this case,

$$w_{QMI} = c[QMI]_0(\ln[QMI]_0 + a).$$

RESULTS AND DISCUSSION

The reaction of QMI with QH_2 consists in the reduction of one of the reactants (QMI) due to the oxidation of the other (QH_2). The products are $QMIH_2$ and 2,5-di-*tert*-butyl-1,4-quinone (Q):



QMI QH_2 $QMIH_2$ Q

The reaction has a complex mechanism, as indicated by the following two specific features of its kinetics: (a) fractional orders of the reaction with respect to components and (b) a continuous increase in the second-order rate constant in the course of the reaction [1, 4]. The chain mechanism of the reaction was demonstrated by the addition of an initiator (tetraphenylhydrazine). Thus, at 298.2 K, an increase in the rate of initiation by ~10^{-9} mol l^{-1} s^{-1} due to the initiator resulted in an increase in the rate of reaction by ~10^{-6} mol l^{-1} s^{-1}; hence, it follows that the chain length is several thousands of units. The mechanism of the (uncatalyzed) reaction is presented below in Scheme 1 [1, 4].

$QMI + QH_2 \longrightarrow QMIH^{\cdot} + QH^{\cdot}$	Chain initiation	(I)
$QMI + QH^{\cdot} \longrightarrow QMIH^{\cdot} + Q$	Chain propagation	(II)
$QMIH^{\cdot} + QH_2 \longrightarrow QMIH_2 + QH^{\cdot}$	Chain propagation	(III)
$QMIH^{\cdot} + QMIH^{\cdot} \longrightarrow QMI + QMIH_2$	Chain termination	(IV)
$QMIH^{\cdot} + QH^{\cdot} \longrightarrow QMI + QH_2\ (QMIH_2 + Q)$	Chain termination	(V)
$QH^{\cdot} + QH^{\cdot} \longrightarrow Q + QH_2$	Chain termination	(VI)

Scheme 1.

In Scheme 1, $QMIH^{\cdot}$ and $QH^{\cdot}$ designate the semiquinone radicals formed by hydrogen abstraction from $QMIH_2$ and QH_2, respectively. Actually, two types of $QMIH^{\cdot}$ radicals can be generated from $QMIH^{\cdot}$, 4-hydroxydiphenylaminyl and 4-anilinophenoxyl. This considerably complicates the kinetic interpretation of experimental data, and the problem of the distinguishability of $QMIH^{\cdot}$ radicals will be considered below.

In a kinetic study of the reaction of QMI with QH_2, the numerical values of the rate constants of elementary steps at 298.2 and 340.0 K were found [4]. These data will be used in the subsequent calculations; therefore,

they are given below together with the values of k at 321.5 K calculated from the temperature dependence:

k_i, $l\ mol^{-1}\ s^{-1}$	T, K		
	298.2	321.5*	340.0
k_1	3.22×10^{-3}	2.23×10^{-2}	8.61×10^{-2}
k_2	3.47×10^{7}	1.93×10^{7}	1.28×10^{7}
k_3	1.65×10^{7}	1.71×10^{7}	1.75×10^{7}
$k_4 = k_5$	8×10^{8}	8×10^{8}	8×10^{8}
k_6	4×10^{7}	4×10^{7}	4×10^{7}

* Calculated from the temperature dependence of k.

Kinetic regularities of the catalytic effect of aromatic amines. Data given in Table 1 indicate that the addition of aromatic amines (AmH) significantly affects the rate of the reaction. In the majority of cases, a monotonic increase or, in contrast, a decrease in the rate with increasing amine concentration was observed; the form of w_{QMI} as a function of [AmH] depends on the ratio [QMI]/[QH_2] (Fig. 1). Figure 2 demonstrates that, in some cases, the graph of w_{QMI} plotted against [AmH] has the shape of a curve with a minimum whose depth and coordinates depend on the concentrations of QMI and QH_2. It was reasonable to assume that only the descending or ascending branch of such a curve, which is generally more complicated, was observed in the majority of experiments (Table 1).

In addition to the six steps shown in Scheme 1, the mechanism of the reaction of QMI with QH_2 in the presence of AmH also includes the following elementary steps with the participation of AmH and its aminyl radical $Am^{\cdot}$ [2]:

$QMI + AmH \longrightarrow QMIH^{\cdot} + Am^{\cdot}$	Chain initiation – 2	(VII)
$Am^{\cdot} + QH_2 \rightleftharpoons AmH + QH^{\cdot}$	Radical	(VIII), (–VIII)
$QMIH^{\cdot} + AmH \longrightarrow QMIH_2 + Am^{\cdot}$	exchange	(IX)
$QMIH^{\cdot} + Am^{\cdot} \longrightarrow QMI + AmH$	Chain	(–VII)
$QH^{\cdot} + Am^{\cdot} \longrightarrow Q + AmH$	termination – 2	(X)
$Am^{\cdot} + Am^{\cdot} \longrightarrow$ Products	Chain termination	(XI)

Scheme 2.

According to this mechanism, both additional step (VII) of chain initiation and new steps (–VII), (X), and (XI) of chain termination occurred in the system in the presence of amines. Step (VII) increased the rate of the chain reaction, whereas steps (–VII), (X), and (XI) inhibited the process. Reaction (XI) was not previously considered. However, this reaction takes into account the irreversible consumption of the AmH catalyst; therefore, it is of particular interest.

The presented mechanism takes into account the most important well-known reactions with the participation of the reactants and catalysts. It is believed that this mechanism is universal; that is, it can be used to explain the catalytic effect of all of the test aromatic amines at any concentration and temperature.

To test this hypothesis, experimental data in Table 1 should be compared with the reaction rates w_{QMI} calculated using an equation derived from the proposed mechanism. To obtain this equation in explicit form, the chain reaction mechanism should be taken into account. An attempt to use a more accurate quasi-steady-state approximation for this purpose ran into serious mathematical problems because the mechanism includes six bimolecular steps of radical decay.

Let us write steady-state equations for the $QMIH^{\cdot}$ and $QH^{\cdot}$ radicals with consideration for only rapidly occurring steps (II) and (III) of chain propagation and steps (VIII), (–VIII), and (IX) of radical exchange, whereas the rates of other steps are ignored:

$$d[QMIH^{\cdot}]/dt = k_2[QMI][QH^{\cdot}] - (k_3[QH_2] + k_9[AmH])[QMIH^{\cdot}] = 0, \quad (1)$$

$$d[QH^{\cdot}]/dt = (k_3[QMIH^{\cdot}] + k_8[Am^{\cdot}])[QH_2] - (k_2[QMI] + k_{-8}[AmH])[QH^{\cdot}] = 0. \quad (2)$$

At long chains, QMI is mainly consumed at step (II) of chain propagation:

$$w_{QMI} = k_2[QMI][QH^{\cdot}]. \quad (3)$$

With the use of Eqs. (1)–(3), we express the concentrations of all the radicals in terms of w_{QMI}:

$$[QH^{\cdot}] = \frac{w_{QMI}}{k_2[QMI]}, \quad (4a)$$

$$[QMIH^{\cdot}] = \frac{w_{QMI}}{k_3[QH_2] + k_9[AmH]} = \frac{k_2[QMI]}{k_3[QH_2] + k_9[AmH]}[QH^{\cdot}], \quad (4b)$$

Table 1. Experimental data on the catalytic effect of secondary aromatic amines AmH on the chain reaction of QMI with QH_2

Series no.	T, K	[QMI] × 10^4, mol/l	[QH_2] × 10^4, mol/l	[AmH] × 10^3, mol/l	$w_{QMI} \times 10^6$, mol l^{-1} s^{-1}
AmH = 4,4'-Dimethoxydiphenylamine					
1	298.2	2.0	2.0	0	1.090
				0.20	0.860
				0.60	0.769
				1.00	0.698
				2.00	0.633
				6.00	0.644
2	321.5	1.95	0.488	0	0.388
				0.584	0.410
				1.95	0.481
3	″	″	0.244	0	0.145
				0.195	0.208
				0.585	0.232
				1.95	0.298
				5.85	0.367
				11.70	0.577
4	340.0	1.90	0.95	0	1.75
				0.19	1.63
				0.57	1.45
				1.90	1.80
				5.70	1.84
				11.40	2.01
5	″	″	0.475	0	0.708
				0.19	0.679
				0.57	0.812
				1.90	1.160
				5.70	1.540
				11.40	1.620
6	″	″	0.238	0	0.265
				0.19	0.322
				0.57	0.420
				1.90	0.570
				5.70	0.960
				11.40	1.21
7	″	0.95	″	0	0.182
				0.19	0.216
				0.57	0.270
				1.90	0.318
				5.70	0.418
8	″	″	0.95	0	1.060
				0.19	0.844
				0.57	0.720
				1.90	0.676
				5.70	0.578
				11.40	0.711

Table 1. (Contd.)

Series no.	T, K	[QMI] × 10^4, mol/l	[QH_2] × 10^4, mol/l	[AmH] × 10^3, mol/l	$w_{QMI} \times 10^6$, mol l^{-1} s^{-1}
AmH = 4-Methoxydiphenylamine					
9	298.2	2.0	6.0	0	4.42
				2.0	3.76
				12.0	2.81
				24.0	2.58
10	321.5	1.95	0.244	0	0.146
				1.95	0.181
				5.85	0.240
				11.70	0.314
11	340.0	1.90	0.238	0	0.265
				1.90	0.432
				5.70	0.603
				11.40	0.860
12	″	″	0.475	0	0.708
				1.90	0.814
				5.70	0.943
AmH = 4,4'-Dimethyldiphenylamine					
13	298.2	2.0	6.0	0	4.42
				2.0	3.65
				6.0	2.88
				12.0	3.03
				24.0	2.34
14	321.5	1.95	0.244	0	0.145
				1.95	0.190
				5.85	0.247
				11.70	0.307
15	340.0	1.90	0.475	0	0.708
				1.90	0.868
				5.70	1.040
				11.40	1.310
16	″	″	0.238	0	0.265
				1.90	0.385
				5.70	0.553
				11.40	0.750
AmH = Dimethyldi-(4-phenylaminophenoxy)silane*					
17	321.5	1.95	0.244	0	0.145
				1.95	0.209
				5.85	0.387
				11.70	0.453
18	340.0	1.90	0.475	0	0.708
				0.57	0.745
				1.90	0.958
				5.70	1.360
19	″	″	0.238	0	0.265
				0.57	0.342
				1.90	0.450
				5.70	0.783

Table 1. (Contd.)

Series no.	T, K	$[QMI] \times 10^4$, mol/l	$[QH_2] \times 10^4$, mol/l	$[AmH] \times 10^3$, mol/l	$w_{QMI} \times 10^6$, mol l^{-1} s^{-1}
20	″	0.95	″	0	0.182
				0.57	0.177
				1.90	0.300
				5.70	0.417
AmH = Diphenylamine					
21	298.2	2.0	4.0	0	2.70
				0.2	2.80
				1.0	2.74
				4.0	2.75
				11.8	2.63
				47.1	2.50
22	340.0	1.90	0.475	0	0.708
				5.7	0.803
				11.4	0.827
				22.8	0.866
23	″	″	0.238	0	0.265
				5.7	0.347
				11.4	0.293
				22.8	0.431
AmH = 4,4'-Dibromodiphenylamine					
24	340.0	1.9	0.475	0	0.708
				5.7	0.776
				11.4	0.813
				22.8	0.868
25	″	″	0.238	0	0.265
				5.7	0.311
				11.4	0.351
				22.8	0.425

Note: Reaction conditions, chlorobenzene and bubbling argon.
*$(C_6H_5–NH–C_6H_4–O)_2Si(CH_3)_2$.

$$[Am^{\cdot}] = w_{QMI}[AmH] \times \frac{k_2k_9[QMI] + k_{-8}(k_3[QH_2] + k_9[AmH])}{k_2k_8[QMI][QH_2](k_3[QH_2] + k_9[AmH])}. \quad (4c)$$

Equation (4b) is an analog of the equation of long chains. For the catalytic chain reaction under consideration, a linear relationship between the concentrations of $QMIH^{\cdot}$ and $QH^{\cdot}$ radicals, which propagate the chain, was retained; however, the proportionality factor depends not only on the concentrations of the QMI and QH_2 components of the chain reaction but also on the concentration of the AmH catalyst.

Let us write an equation for steady-state reaction conditions:

$$(k_1[QH_2] + k_7[AmH])[QMI] = k_4[QMIH^{\cdot}]^2 + k_5[QMIH^{\cdot}][QH^{\cdot}] + k_6[QH^{\cdot}]^2 + (k_{-7}[QMIH^{\cdot}] + k_{10}[QH^{\cdot}] + k_{11}[Am^{\cdot}])[Am^{\cdot}]. \quad (5)$$

Substituting expressions (4a)–(4c) into Eq. (5), we obtain the following equation for the rate of reaction in explicit form:

$$w_{QMI}^2 = \frac{k_2^2k_8^2[QH_2]^2[QMI]^3A^2B}{k_2^2[QMI]^2C + k_2[QMI]AD + A^2E}, \quad (6)$$

where

$$A = k_3[QH_2] + k_9[AmH],$$

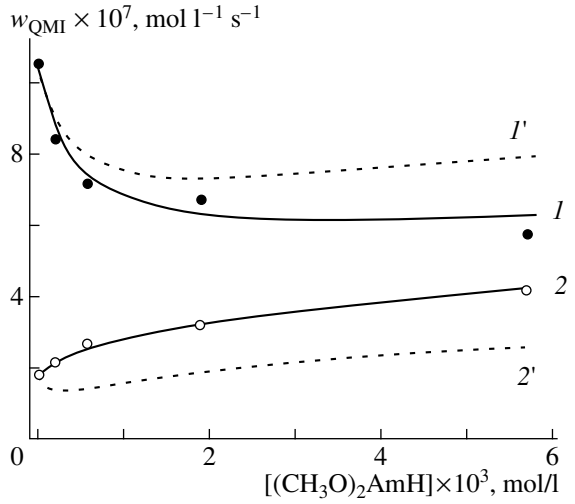


Fig. 1. Dependence of the initial reaction rate on the concentration of 4,4'-dimethoxydiphenylamine. Solvent, chlorobenzene; $T = 340$ K. [QMI] and [QH_2], mol/l × 10^4: (*1* and *1'*) 0.95 and 0.95; (*2* and *2'*) 0.95 and 0.238, respectively. Points indicate experimental data and dashed lines show the results of calculations by Eq. (6) with the use of all values of k from Table 2 and the values of k_7, k_8, k_{-8}, and k_9 from Table 3.

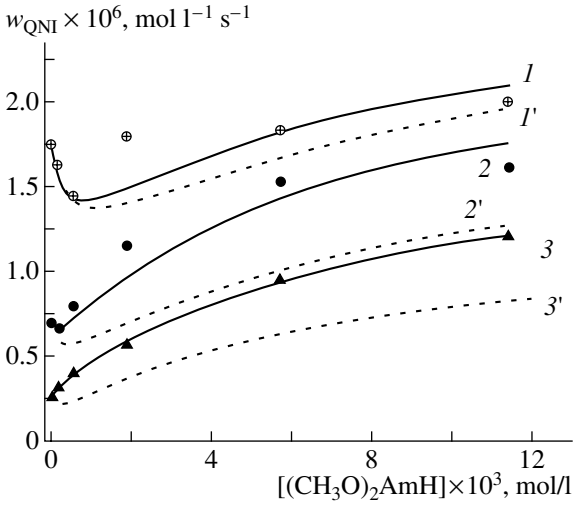


Fig. 2. Changes in the initial rate of reaction as a function of the concentration of 4,4'-dimethoxydiphenylamine at $[QMI]_0 = 1.90 \times 10^{-4}$ mol/l. [QH_2], mol/l × 10^5: (*1*, *1'*) 9.50, (*2*, *2'*) 4.75, and (*3*, *3'*) 2.38. Solvent, chlorobenzene; T = 340 K. Points indicate experimental data and dashed lines (*1'*–*3'*) show the results of calculations by Eq. (6) with the use of all the values of k from Table 2. Solid lines (*1*–*3*) are obtained by calculation using Eq. (6) and the values of k_7, k_8, k_{-8}, k_9 from Table 3 and other values from Table 2.

$$B = k_1[QH_2] + k_7[AmH],$$

$$C = k_4k_8^2[QH_2]^2 + k_{-7}k_8k_9[QH_2][AmH] + k_9^2k_{11}[AmH]^2,$$

$$D = k_5k_8^2[QH_2]^2 + k_8(k_{-7}k_{-8} + k_9k_{10})[QH_2][AmH] + 2k_{-8}k_9k_{11}[AmH]^2, \quad \text{and}$$

$$E = k_6k_8^2[QH_2]^2 + k_8k_{-8}k_{10}[QH_2][AmH] + k_{-8}^2k_{11}[AmH]^2.$$

As noted above, the rate constants of elementary steps in Scheme 2 can be satisfactorily calculated from the equations of the parabolic model of a transition state. The accuracy of these calculations is reasonable for this work; usually, the calculated and experimental values of k differed by a factor of 1.5–2 or lower. First, data on the dissociation energies of ruptured and formed bonds are required for the calculations. The NH bond energies in amines (AmH) were taken from [3]. The strength of the O–H bond in QH_2 was estimated recently: $D_{OH}(QH_2)$ = 337.3 ± 2.3 kJ/mol [6]. Let us assume that the dissociation energy of the OH bond in the $QH^{\bullet}$ radical is equal to that in the simplest 4-hydroxyphenoxyl radical: D_{OH} = 226.1 kJ/mol [3]. Finally, we will use in the calculations the following recently evaluated strengths of O–H and N–H bonds in $QMIH_2$ and 4-hydroxydiphenylaminyl C_6H_5–$N^{\bullet}$–C_6H_4–OH ($^{\bullet}$N(QMI)OH) and 4-anilinophenoxyl C_6H_5–NH–C_6H_4–$O^{\bullet}$ (NH(QMI)$O^{\bullet}$) radicals generated from $QMIH_2$ [6], kJ/mol:

$$D_{OH}(QMIH^{\bullet}) = D_{OH}(^{\bullet}N(QMI)OH) = 259.5,$$

$$D_{NH}(QMIH^{\bullet}) = D_{NH}(HN(QMI)O^{\bullet}) = 273.6,$$

$$D_{OH}(QMIH_2) = 339.1, \quad \text{and}$$

$$D_{NH}(QMIH_2) = 353.2.$$

Consideration of the dual nature of $QMIH^{\bullet}$ radicals. Quinone monoimine is a bifunctional compound and participates in the reactions of H-atom abstraction and attachment at either its oxygen atom or the nitrogen atom to form the $^{\bullet}$N(QMI)OH aminyl radicals and the HN(QMI)$O^{\bullet}$ phenoxyl radicals, respectively. The reactivity of these two types of $QMIH^{\bullet}$ radicals can be significantly different. Because of this, in a rigorous interpretation, the number of elementary steps in Schemes 1 and 2 should be significantly increased. In this case, mathematical problems increase so that an analysis of the mechanism and an interpretation of experimental data become practically impossible.

The problem can be simplified considering that O–H bonds are weaker than N–H bonds in $QMIH_2$ and the $QMIH^{\bullet}$ radical and that the fraction of relatively inactive $^{\bullet}$O(QMI)NH phenoxyl radicals in the total

concentration of $QMIH^{\bullet}$ radicals during the reaction is greater than the fraction of $^{\bullet}N(QMI)OH$ aminyl radicals. Thus, because the difference in the dissociation energies of the OH bonds in $QMIH_2$ is small, the formation of the $^{\bullet}O(QMI)NH$ phenoxyl radicals in fast step (II) of chain propagation is preferable to the formation of the $^{\bullet}N(QMI)OH$ aminyl radicals in this reaction. In contrast, the $^{\bullet}N(QMI)OH$ aminyl radicals are more active in fast reactions (III) and (IX), in which the $QMIH^{\bullet}$ radicals are consumed; this contributes to a decrease in their fraction in the total concentration of $QMIH^{\bullet}$.

There is another argument in favor of the above assumption on the concentration ratio between the radicals: this is the following rapid bimolecular isomerization reaction of the aminyl and phenoxyl radicals with the participation of quinone imine QMI (for clarity, it is designated by O(QMI)N):

$$\left.\begin{array}{l} {}^{\bullet}N(QMI)OH + O(QMI)N \rightleftharpoons N(QMI)O + {}^{\bullet}O(QMI)NH \\ \text{or in the general form: } QMIH^{\bullet} + QMI \rightleftharpoons QMI + QMIH^{\bullet} \end{array}\right\} \quad \text{(XII), (–XII)}$$

The calculations performed with the use of the method of crossing parabolas demonstrated that the absolute values of k_{12} and k_{-12} are high; for example, at 321.5 K, $k_{12} = 3.0 \times 10^6$ and $k_{-12} = 1.54 \times 10^5$ l mol^{-1} s^{-1} and $K_{12} = k_{12}/k_{-12} = 19.5$. In the general case,

$$K_{12} = \frac{k_{12}}{k_{-12}} = \frac{x}{1-x}$$

$$= \frac{6.07 \times 10^6 \exp(-1.84/RT)}{6.07 \times 10^7 \exp(-15.98/RT)} = 0.1e^{\frac{14.1}{RT}},$$

where x is the fraction of the $^{\bullet}O(QMI)NH$ phenoxyl radicals in the total concentration of the $QMIH^{\bullet}$ semiquinone radicals; the activation energies are expressed in kJ/mol.

Taking into account the above remarks, we will further assume that, at low conversions, when the quinone imine concentration is highest, the concentrations of $^{\bullet}O(QMI)NH$ and $^{\bullet}N(QMI)OH$ radicals are close to thermodynamic equilibrium values determined by the equilibrium constant K_{12}. Under this assumption, the relative fractions of phenoxyl and aminyl radicals in the total $QMIH^{\bullet}$ concentration at different temperatures can be evaluated:

T, K	K	x	$1-x$
298.2	29.5	0.967	0.033
321.5	19.5	0.951	0.049
340.0	14.5	0936	0.064

Note: x and $1-x$ are the fractions of $^{\bullet}O(QMI)NH$ and $^{\bullet}N(QMI)OH$, respectively.

Calculation of the rate constants of reactions with the participation of amines and their radicals using the method of crossing parabolas. According to the method of crossing parabolas [3], all the elementary reactions were subdivided into certain classes; this classification was primarily based on the chemical nature of atoms in a three-centered transition state. Each class of reactions is characterized by a certain set of specific parameters (the activation energy $E_{e,0}$ of thermoneutral reaction, the preexponential factor A_0 on an attacked-bond basis, etc.), which were calculated and tabulated (for example, see [3]).

The form of equations for the calculation of rate constants k depends on the enthalpy ΔH_e, which is calculated with consideration for the zero vibration energies of ruptured (i) and formed (f) bonds in the method of crossing parabolas:

$$\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f).$$

Here, D and ν are the bond dissociation energies and vibration frequencies, respectively; h is Plank's constant; and N_A is Avogadro's number. For each class of reactions, there are two threshold values of $\Delta H_{e,min}$ (exothermic reactions) and $\Delta H_{e,max}$ (endothermic reactions), which were calculated from experimental data and tabulated. If the enthalpy calculated from Eq. (7) is $\Delta H_e < \Delta H_{e,min}$, the activation energy of the reaction is $E = 0.5RT$. If $\Delta H_e > \Delta H_{e,max}$, $E = \Delta H + 0.5RT = D_i - D_f + 0.5RT$. In both cases, the preexponential factor A_0, which is characteristic of a given class of reactions, should be multiplied by the coefficient $\gamma > 1$:

$$\gamma = [1 + 1.3(|\Delta H_e|^{1/2} - |\Delta H_{e,min}|^{1/2})]^2$$

or

$$\gamma = [1 + 1.3(\Delta H_e^{1/2} - \Delta H_{e,max}^{1/2})]^2.$$

Most elementary reactions in Scheme 2 belong to reactions of the above types. For example, let us calculate the rate constant of endothermic reaction (VII) with the participation of unsubstituted diphenylamine (required data were taken from [3]):

$$QMI + Ph_2NH \longrightarrow QMIH^{\bullet} + Ph_2N^{\bullet} \quad \text{(VII)}$$

$$N(QMI)O + Ph_2NH \longrightarrow HN(QMI)O^{\bullet} + Ph_2N^{\bullet}, \text{(VIIa)}$$

$$N(QMI)O + Ph_2NH \longrightarrow {}^{\cdot}N(QMI)OH + Ph_2N^{\cdot}, \text{(VIIb)}$$

$$k_7 = k_{7a} + k_{7b}.$$

For reaction (VIIa): $0.5hN_A(\nu_{NH}-\nu_{NH}) = 0$, $\Delta H_{e,\max(7a)} = 31.2$ kJ/mol, and $A_{0(7a)} = 1 \times 10^8$ l mol^{-1} s^{-1}. The enthalpy of the reaction is $\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f) = 91.1$ kJ/mol $> \Delta H_{e,\max(7a)} = 31.2$ kJ/mol. The activation energy (kJ/mol) is $E_a = D_i - D_f + 0.5RT = 91.1 + 0.5RT$, $\gamma = [1 + 1.3(\Delta H_e^{1/2} - \Delta H_{e,\max}^{1/2})]^2 = [1 + 1.3(91.1^{1/2} - 31.2^{1/2})]^2 = 37.8$; and k_{7a} (l mol^{-1} s^{-1}) $= \gamma A_{0(7a)} e^{-1/2} e^{-91.1/RT} = 2.29 \times 10^9\, e^{-91.2/RT}$. For reaction (VIIb): $0.5hN_A(\nu_{NH}-\nu_{OH}) = -1.5$ kJ/mol, $\Delta H_{e,\max(7b)} = 16.7$ kJ/mol, and $A_{0(7b)} = 1 \times 10^8$ l mol^{-1} s^{-1}. The enthalpy of the reaction is $\Delta H_e = D_i - D_f + 0.5hN_A(\nu_i - \nu_f) = 364.7 - 259.5 - 1.5 = 103.7$ kJ/mol $> \Delta H_{e,\max(7b)} = 16.7$ kJ/mol. The activation energy (kJ/mol) is $E_a = D_i - D_f + 0.5RT = 105.2 + 0.5RT$; $\gamma = [1 + 1.3(103.7^{1/2} - 16.7^{1.2})]^2 = 79.7$; and k_{7b} (l mol^{-1} s^{-1}) $= \gamma A_{0(7b)} e^{-1/2} e^{-105.2/RT} = 4.83 \times 10^9 e^{-105.2/RT}$.

If the enthalpy of reaction ΔH_e falls within the range $\Delta H_{e,\min} - \Delta H_{e,\max}$, somewhat different equations are used for calculating k; these equations were given in [3] together with the corresponding tabulated parameters of such elementary reactions.

The rate constants of elementary steps (Scheme 2) with the participation of all of the amines studied were calculated with the use of the method of crossing parabolas; Table 2 summarizes the results. The calculated dependence of w_{QMI} on [AmH] was obtained by substituting these values of k in Eq. (6) for each series of experiments in Table 1. As can be seen in Figs. 1 and 2 (dashed lines), the initial accuracy of the found rate constants suffices for an adequate description of experimental data; w_{QMI}^{exp} and w_{QMI}^{calcd} differ by a factor of ~2 or lower.

With the use of numerical methods, a new set of k can be chosen, which results in a better fit of the results of calculations to experimental data. For this purpose, data in Table 1 were treated by an iteration method at fixed values of the rate constants of all reactions except for the steps of H-atom abstraction (k_7, k_8, k_{-8}, and k_9). These rate constants were varied over a narrow range: by a factor of no higher than two (or three in rare cases), as compared with the corresponding value in Table 2; this approximately corresponds to the accuracy of the calculation of k by the method of crossing parabolas. Table 3 summarizes the resulting values of k_7, k_8, k_{-8}, and k_9 for all the reaction series. As can be seen in Figs. 1 and 2 (solid lines), with the use of this set of k, the accuracy of the description of experimental data considerably increased up to coincidence between calculated and experimental data.

As can be seen, Eq. (6) accurately describes experimental data for all the amines used as catalysts at different temperatures and reactant and additive concentrations. This is indicative of the correctness of the proposed mechanism of catalysis.

Specific features of the catalytic reaction mechanism. To elucidate the catalytic reaction mechanism, changes in the rates w of elementary steps with amine concentration [AmH] should be studied. For example, let us consider two series of experiments with the participation of 4,4'-dimethoxydiphenylamine, which is the strongest among the catalysts tested (Fig. 3). In one of these series (Fig. 3a), amine additives caused an increase in the rate (series 6 in Table 1); in contrast, in the other series (Fig. 3b), amine additives inhibited the reaction (series 8 in Table 1). The concentrations of radicals were calculated from Eqs. (4a)–(4c) with the use of experimental values of w_{QMI} from Table 1. The rate constants k_7, k_8, k_{-8}, and k_9 were taken from Table 3.

It can be seen in Fig. 3 that the reaction mechanism dramatically changed with increasing amine concentration, as evidenced by the following changes in the rates of elementary steps:

(a) The overall rate of radical formation in the system dramatically increased; this was due to an increase in the rate of reaction (VII) with the participation of AmH, whereas the contribution of step (I) of chain initiation in the initial chain reaction is small, and can be ignored.

(b) Steps (–VII)–(X) with the participation of Am$^{\cdot}$ catalyst radicals became the main reactions of chain termination, whereas the role of steps (IV)–(VI) of chain termination in the uncatalyzed chain reaction became negligibly small.

(c) The rate of step (III) of chain propagation in the initial chain reaction significantly decreased and became negligibly small; in place of this reaction, steps (VIII), (–VIII), and (IX) of radical exchange with the participation of the catalyst and its radical began to occur with increasing intensity.

As can be seen, of all the six steps of the chain reaction of QMI with H_2Q (Scheme 1), only step (II) of chain propagation plays an important role at sufficiently high catalyst concentrations, whereas the rates of the other elementary steps can be ignored. In place of them, new processes with the participation of the catalyst and its radicals come into play. In spite of this strong rearrangement of the mechanism, the reaction of QMI with H_2Q in the presence of a catalyst remains a chain reaction and leads to the formation of the same products as in the absence of the catalyst.

These results provide support for a specific feature of radical processes in systems containing aromatic amines and compounds with relatively weak O–H bonds (phenols, hydroperoxides, etc.), which was noted previously [8]: the tendency of these processes to couple. It can be seen that, in the chain reaction of QMI with H_2Q catalyzed by aromatic amines, two cyclic (chain and catalytic) coupled reactions occur, which

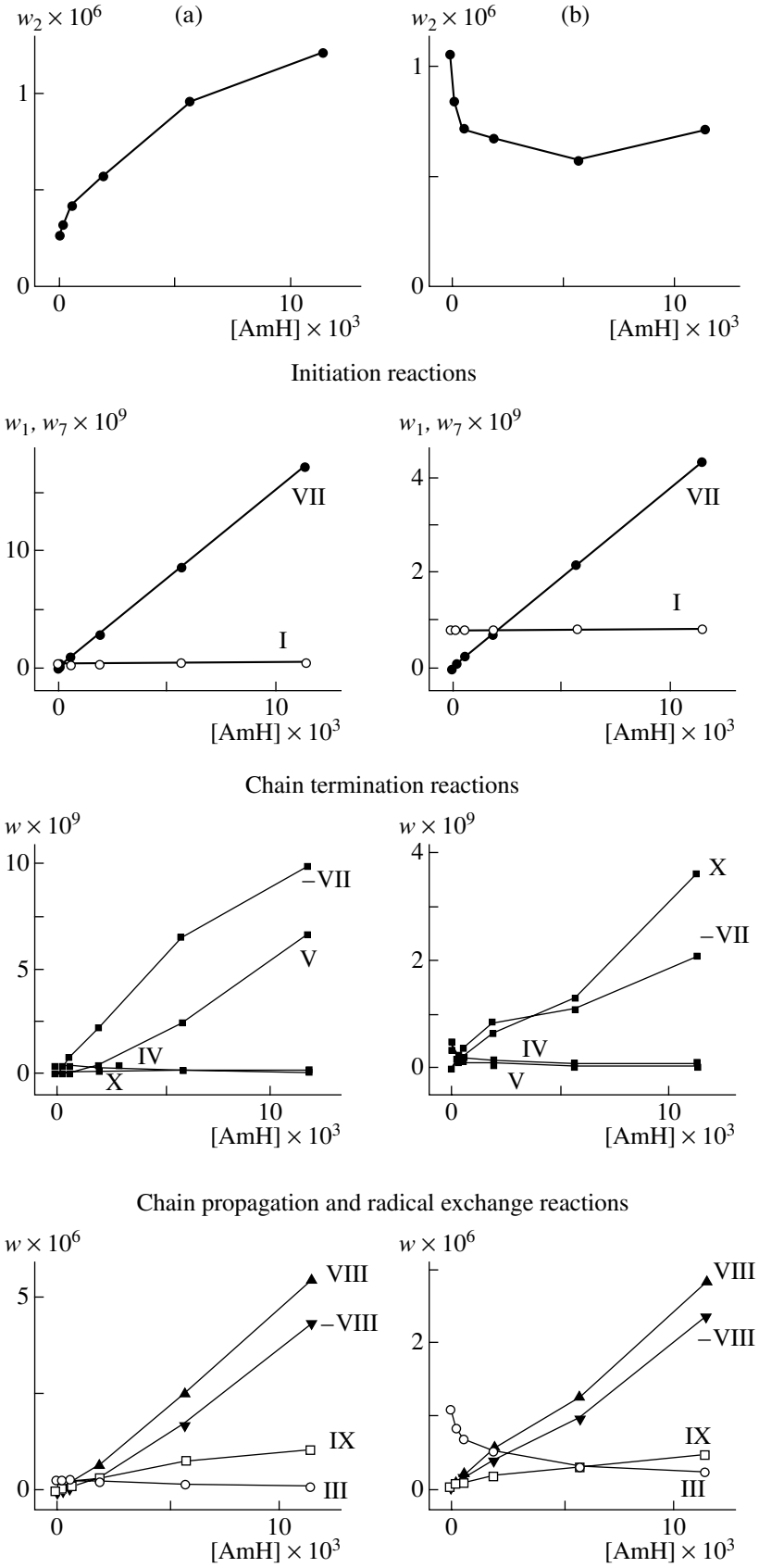


Fig. 3. Changes in the rates of elementary steps (w_i, mol l^{-1} s^{-1}) of the catalytic reaction as functions of the concentration of 4,4'-dimethoxydiphenylamine (mol/l) in reaction series (a) 6 and (b) 8 (see Table 1).

Table 2. Rate constants of elementary steps (numbered in accordance with Schemes 1 and 2) with the participation of 4,4'-substituted diphenylamines (AmH) and the resulting diphenylaminyl radicals ($Am^{\bullet}$) calculated by the method of crossing parabolas

Reaction number	Reaction	k_i, l mol^{-1} s^{-1}	Diphenylamine D_{NH} = 364.7		4,4'-Dibromodiphenylamine D_{NH} = 364.2		4,4'-Dimethyldiphenylamine D_{NH} = 357.5			Dimethyldi-(4-phenylaminophenoxy)silane* D_{NH} = 349.1 [6]		4-Methoxydiphenylamine D_{NH} = 355.9			4,4'-Dimethoxydiphenylamine D_{NH} = 348.6		
			298.2 K	340.0 K	298.2 K	340.0 K	298.2 K	321.5 K	340.0 K	321.5 K	340.0 K	298.2 K	321.5 K	340.0 K	298.2 K	321.5 K	340.0 K
(VII)	QMI + AmH ⟶ QMIH$^{\bullet}$ + Am$^{\bullet}$																
(VIIa)	N(QMI)O + AmH ⟶ HN(QMI)O$^{\bullet}$ + Am$^{\bullet}$	$k_{7a} \times 10^5$	0.0252	2.31	0.0305	2.73	0.388	4.51	24.9	166	773	0.711	7.88	42.1	11.0	98.7	454
(VIIb)	N(QMI)O + AmH ⟶ $^{\bullet}$N(QMI)OH + Am$^{\bullet}$	$k_{7b} \times 10^7$	0.0180	3.32	0.0219	3.94	0.295	5.18	38.1	209	1290	0.549	9.20	65.4	9.23	125	766
		$k_7 = (k_{7a} + k_{7b}) \times 10^5$	0.0254	2.34	0.0307	2.77	0.91	4.56	25.3	168	786	0.716	7.97	42.7	11.1	100	462
		$k_{7,exp} \times 10^5$							38 ± 15	132 ± 40	800 ± 320						410 ± 140
(VIII)	Am$^{\bullet}$ + QH$_2$ ⟶ AmH + HQ$^{\bullet}$ **	$k_8 \times 10^{-7}$	6.53		6.17		2.13			0.406	0.431	1.63			0.34	0.37	0.40
(–VIII)	QH$^{\bullet}$ + AmH ⟶ QH$_2$ + Am$^{\bullet}$	$k_{-8} \times 10^{-4}$	0.510	1.99	0.590	2.24	3.01	5.43	8.19	48.5	65.6	3.78	6.52	9.52	17.5	26.8	36.0
(IX)	QMIH$^{\bullet}$ + AmH ⟶ QMIH$_2$ + Am$^{\bullet}$																
(IXa)	$^{\bullet}$O(QMI)NH + AmH ⟶ HO(QMI)NH + Am$^{\bullet}$	$k_{9a} \times 10^{-4}$	0.851	3.03	0.976	3.39	3.86	6.61	9.62	68.9	91.3	5.35	8.91	12.7	25.5	38.0	50.0

Table 2. (Contd.)

Reaction number	Reaction	k_i, 1 mol^{-1} s^{-1}	Diphenylamine D_{NH} = 364.7		4,4'-Dibromodiphenylamine D_{NH} = 364.2		4,4'-Dimethyldiphenylamine D_{NH} = 357.5			Dimethyldi-(4-phenylaminophenoxy)silane* D_{NH} = 349.1 [6]		4-Methoxydiphenylamine D_{NH} = 355.9			4,4'-Dimethoxydiphenylamine D_{NH} = 348.6		
			298.2 K	340.0 K	298.2 K	340.0 K	298.2 K	321.5 K	340.0 K	321.5 K	340.0 K	298.2 K	321.5 K	340.0 K	298.2 K	321.5 K	340.0 K
(IXb)	HO(QMI)N$^{\bullet}$ + AmH ⟶ HO(QMI)NH + Am	$k_{9b} \times 10^{-4}$	2.06	5.49	2.29	6.04	9.56	15.3	21.1	147	187	14.7	22.8	30.9	57.4	80.5	102
		$k_9 = xk_{9a} + (1-x)k_{9b} \times 10^{-4}$	0.891	3.19	1.02	3.56	4.05	7.04	10.5	72.7	97.4	5.64	9.59	13.9	26.6	40.1	53.3
(–VII)	QMIH$^{\bullet}$ + Am$^{\bullet}$ ⟶ QMI + AmH																
(–VIIa)	$^{\bullet}$O(QMI)NH + Am$^{\bullet}$ ⟶ O(QMI)N + AmH	$k_{-7a} \times 10^{-9}$	2.29		2.27		1.93			1.54		1.86			1.51		
(–VIIb)	HO(QMI)N$^{\bullet}$ + Am$^{\bullet}$ ⟶ O(QMI)N + AmH	$k_{-7b} \times 10^{-8}$	4.85		4.81		4.36			3.79		4.25			3.76		
		$k_{-7} = xk_{-7a} + (1-x)k_{-7b} \times 10^{-9}$	2.20		2.18		1.86			1.48		1.79			1.45		
(X)	QH$^{\bullet}$ + Am$^{\bullet}$ ⟶ Q + AmH	$k_{10} \times 10^{-8}$	7.24		7.20		6.71			6.11		6.60			6.07		
(XI)	Am$^{\bullet}$ + Am$^{\bullet}$ ⟶ Products***	$k_{11} \times 10^{-6}$	13.5		30.0		1.15			2.75		3.0			1.15		

Note: D_{NH} is the dissociation energy of N–H bonds in aromatic amines, kJ/mol [3].
* $(C_6H_5–NH–C_6H_4O)_2Si(CH_3)_2$; the values of k_7, k_{-8}, and k_9 are given in terms of a molecule (two NH groups).
** In terms of a molecule QH_2 (two OH groups).
*** Experimental data taken from [7]; error, ±10%.

Table 3. Optimized values of the rate constants of reactions (VII), (VIII), (–VIII), and (IX) (l mol^{-1} s^{-1}) obtained by the treatment of experimental data in Table 1 using an iteration method

Series no.*	T, K	$k_7 \times 10^5$	$k_8 \times 10^{-7}$	$k_{-8} \times 10^{-4}$	$k_9 \times 10^{-4}$
4,4'-Dimethoxydiphenylamine					
1	298.2	12.0	0.256	56.0	62.3
2	321.5	121	0.587	28.2	18.8
3	″	131	0.590	32.1	22.0
4	340.0	570	0.488	59.1	78.4
5	″	692	0.643	58.0	74.1
6	″	794	1.06	76.9	30.0
7	″	860	1.00	52.5	10.0
8	″	399	0.301	35.6	29.0
4-Methoxydiphenylamine					
9	298.2	0.383	0.405	9.95	9.07
10	321.5	13.0	2.02	7.53	5.53
11	340.0	27.0	3.88	8.18	24.2
12	″	34.0	3.66	17.9	13.0
4,4'-Dimethyldiphenylamine					
13	298.2	0.53	0.806	31.6	9.92
14	321.5	6.0	3.59	3.19	5.84
15	340.0	34.0	4.28	14.5	16.6
16	″	25.0	4.19	10.7	18.0
Dimethyldi-(4-phenylaminophenoxy)silane					
17	321.5	195	0.236	64.8	93.9
18	340.0	973	0.619	76.7	50.3
19	″	740	0.575	47.6	30.7
20	″	890	0.343	40.2	112
Diphenylamine					
21	298.2	0.010	2.0	0.96	0.68
22	340.0	1.0	4.50	3.71	4.61
23	″	3.0	6.71	1.01	1.44
4,4'-Dibromodiphenylamine					
24	340.0	2.0	5.83	2.30	2.25
25	″	3.0	4.81	2.04	2.46

* See Table 1.

manifest themselves simultaneously at all steps of the chain reaction.

An attempt to elucidate which reaction in the QMI + H_2Q + AmH system induces the occurrence of another reaction provides an opportunity to find which component plays the role of actor, inductor, and scavenger. Note that aromatic amines do not react with hydroquinone H_2Q. On the contrary, quinone imine reacts with H_2Q (this is the initial chain reaction) but practically does not react with AmH: the reactant concentrations in QMI + AmH binary systems remained practically unchanged for a long time. This result seems inconsistent with data given in Tables 2 and 3, which are indicative of high rate constants of reaction (VII) between QMI and AmH. The reason for the experimentally observed absence of the interaction of QMI and AmH lies in the reversibility of the reaction. It can be seen in Table 2 that the rate constants k_{-7} of a reverse reaction are higher than k_7 by 12 to 13 orders of magnitude; that is, in the QMI + AmH system, reactions (VII) and (–VII) occur in a near-equilibrium state, which is almost completely shifted toward the initial substances. On the addition of H_2Q to the QMI + AmH binary system, the $QMIH^{\cdot}$ and $Am^{\cdot}$ radicals, which are formed in reaction (VII), are scavenged; in this case, the equilibrium of reactions (VII) and (–VII) is disturbed. Thus, in the QMI + H_2Q + AmH ternary system, QMI plays the role of an actor, the AmH aromatic amine is an inductor (in spite of the apparent absence of the reaction between QMI and AmH), and H_2Q acts as a scavenger. The initial rapidly occurring chain reaction of QMI with H_2Q becomes simultaneously induced in the presence of AmH; it changes its rate because of the simultaneous occurrence of the reaction of QMI with AmH in the system. Because the concentration of the AmH inductor remains practically unchanged in the course of the experiment, the induction factor is very great; consequently, AmH should be considered as a catalyst and the reaction of QMI with H_2Q in the presence of AmH should be considered as a catalyzed reaction.

The mechanism of the amine-catalyzed chain reaction of QMI with H_2Q is different from other coupled chain processes, for example, cooxidation [9] (the R^1H + R^2H + O_2 system, where R^1H and R^2H are cooxidized substances, can also be considered as a ternary system, that is, analogous to the QMI + H_2Q + AmH system). First, each of the cooxidized components (R^1H and R^2H) can undergo oxidation by a chain mechanism, although at a low rate. As for the catalytic chain reaction of QMI with H_2Q, it was noted above that QMI reacts with only one of the components (H_2Q); however, QMI does not react with AmH. Second, in the cooxidation reaction, either of the two participants (R^1H and R^2H) is not only involved in the overall process but also consumed in this process (primarily, in the acts of chain propagation) with a greater or smaller rate to form oxidation products. In the case of the chain reaction of QMI with H_2Q catalyzed by amines, AmH is also actively involved in the overall process; however, in this case, AmH is not consumed because all the reactions of intermediate $Am^{\cdot}$ aminyl radicals generated from AmH (in particular, at the stage of chain propagation) lead exclusively to the regeneration of parent AmH.

Thus, the catalytic chain reaction under discussion in the QMI + H_2Q + AmH system can be considered as a limiting case of other coupled chain processes, in the course of which one of the components is not consumed. At the same time, although the AmH component is not consumed in a coupled reaction, it is actively involved in the overall chain process, has a regulating effect on the rate of this process, and therefore controls the chain process.

REFERENCES

1. Varlamov, V.T., *Dokl. Akad. Nauk*, 1993, vol. 332, no. 4, p. 457.
2. Varlamov, V.T., *Dokl. Akad. Nauk*, 1995, vol. 345, no. 3, p. 339.
3. Denisov, E.T. and Denisova, T.G., *Handbook of Antioxidants*, Boca Raton: CRC, 2000.
4. Varlamov, V.T., *Kinet. Katal.*, 2001, vol. 42, no. 6, p. 836.
5. Stroh, R., Seydel, R., and Hahn, W., *Angew. Chem.*, 1957, vol. 69, no. 22, p. 699.
6. Varlamov, V.T., *Izv. Akad. Nauk, Ser. Khim.*, 2004, no. 2, p. 293.
7. Efremkina, E.A., Khudyakov, I.V., and Denisov, E.T., *Khim. Fizika*, 1987, vol. 6, no. 9, p. 1289.
8. Varlamov, V.T., *Kinet. Katal.*, 2000, vol. 41, no. 3, p. 353.
9. Kucher, R.V. and Opeida, I.A., *Sookislenie organicheskikh veshchestv v zhidkoi faze* (Cooxidation of Organic Compounds in the Liquid Phase), Kiev: Naukova Dumka, 1989.