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The regularities of reversible chain reactions in the equilibrium state

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The characteristics of dynamic equilibrium states in the experimentally studied reversible chain reactions of quinoneimines with hydroquinones and in some reversible chain reactions with similar mechanisms are discussed. The concentrations of radicals and non-radical participants were calculated. The equilibrium concentrations of the same reaction participants depend only on the initial reactant concentrations, being independent of the number of chain initiation—chain termination steps in the reaction mechanism. The results of mathematical modeling of reversible chain reactions using the experimentally determined rate constants for elementary steps of a reaction in the quinoneimine—hydroquinone system are presented. Expressions relating the equilibrium constants of elementary steps to each other and to the equilibrium constant of the total stoichiometric reaction are derived. Examples of other actual reversible chain reactions are presented, indicating that such reactions are widespread.

Key words: reversible chain reactions, elementary steps, equilibrium state, equilibrium concentrations, mechanisms, rate constants, equilibrium constants.

Chain reactions are usually accompanied by a considerable decrease in the free energy; therefore, most of them can be considered as almost irreversible processes, *viz.*, $K_{eq} = \exp(-\Delta G/RT) >> 1$. However, reversible chain reactions characterized by $K_{eq} \approx 1$ are also known. They were initially observed in the gas phase.[1,2] As a rule, gas-phase reversible chain reactions are accompanied by side processes, although some exceptions are known, *e.g.*, the reaction $H_2 + D_2 \rightleftarrows 2\ HD$.[1—3] The reaction rates depend in a complex manner on the temperature and pressure, as well as on the shape and size of the reaction vessel and the concentration of inert diluent gas.[4—6]

Liquid-phase reversible chain reactions were discovered quite recently, when the experimental data on "living" radical polymerization[7—9] and pioneering studies on the chain mechanism of reversible reactions in the quinoneimine—hydroquinone systems[10,11] were reported. The regularities of "living" polymerization are well documented;[12—16] therefore, below we will consider only the reversible chain reactions described by the classical kinetic scheme including the chain initiation, chain propagation, and chain termination steps involving radicals acting as chain carriers.

As time passes, all reversible reactions reach an equilibrium state and stay there for an infinitely long period of time if no external factors are involved. This also concerns reversible chain reactions. In the present study, we elucidate for the first time the dynamic equilibrium states of reversible chain reactions by comparing a number of chain mechanisms.

Reversible chain reactions in quinoneimine—hydroquinone systems. The kinetics of reversible chain reactions of quinoneimines with hydroquinones was studied experimentally; therefore, we will pay particular attention to them. These reactions are described by the following stoichiometric equation[10,11]

$$H_2A + B \rightleftharpoons A + H_2B. \qquad (s), (-s)$$

It can be treated as the simplest mechanism of quinoneimine reactions with hydroquinones. The rate constants k_s and k_{-s} have no physical meaning; however, the ratio k_s/k_{-s} is the actual equilibrium reaction constant K_{eq} which can also be expressed through the equilibrium concentrations of reactants and products*

$$K_{eq} = \frac{k_s}{k_{-s}} = \frac{[H_2B]_{eq}[A]_{eq}}{[B]_{eq}[H_2A]_{eq}}. \qquad (1)$$

Equations (s), (−s) can be used to describe some other reversible reactions including chain processes. Since experimental data are currently available only for the reactions of quinoneimines with hydroquinones, below we will compare different kinetic schemes using the following procedure. First, equilibria in the quinoneimine—hydroquinone systems will be considered. Then, new kinetic schemes will be constructed and analyzed by successive exclusion of some elementary steps from the mechanism of quinon-

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* Below all reactions are considered in the equilibrium state only; therefore, the subscripts "eq" at the concentrations are omitted.

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eimine reactions with hydroquinones. Particular steps will be excluded in such a manner that the stoichiometric equations of the reactions thus derived be consistent with the equations (s), (–s). In this case, all mechanisms will be characterized by the same equilibrium constant K_{eq}. Finally, we assume that the reaction begins at the instant of mixing of the initial reactants H_2A and B taken in the initial concentrations $[H_2A]_0$ and $[B]_0$ that are the same in all mechanisms. This will simplify our comparison of different kinetic schemes, because the equilibrium concentrations of the same non-radical substances H_2A, B, A, and H_2B will also be the same for all mechanisms.

The kinetics of a reversible chain reaction of 2,5-dichlorohydroquinone (H_2A) with *N*-phenyl-1,4-benzoquinonemonoimine (B) resulting in 2,5-dichloroquinone (A) and 4-hydroxydiphenylamine (H_2B) (Scheme 1) was studied.[17,18]

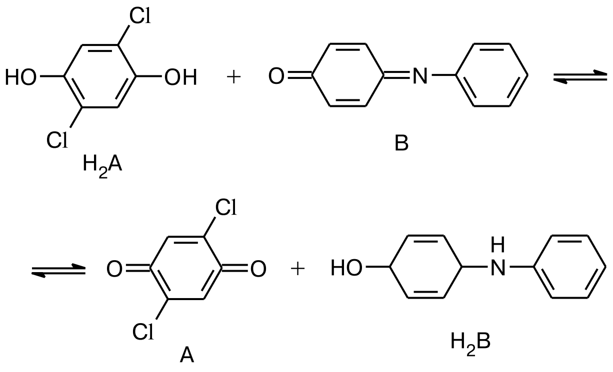
The rate constants for elementary steps of this reaction used in the present study are listed in Table 1.

The mechanism of quinoneimine reactions with hydroquinones is presented in the kinetic Scheme 2.[10,11]

Here, $HB^{\cdot}$ denotes the semiquinone radicals produced upon abstraction of H atom from 4-hydroxydiphenylamine (H_2B) or upon addition of an H atom to quinoneimine (B). These can be both 4-oxydiphenylaminyl and 4-anilinophenoxyl radicals ($HO—C_6H_4—N^{\cdot}—C_6H_5$ and $^{\cdot}O—C_6H_4—NH—C_6H_5$, respectively); for the sake of simplicity, the difference between them is not considered.

Some time after the reaction started, the rates of the direct and appropriate reverse steps (see Scheme 2) become

Scheme 1



Scheme 2

$$B + H_2A \rightleftharpoons HA^{\cdot} + HB^{\cdot} \quad (1), (-1)$$

$$B + HA^{\cdot} \rightleftharpoons HB^{\cdot} + A \quad (2), (-2)$$

$$HB^{\cdot} + H_2A \rightleftharpoons H_2B + HA^{\cdot} \quad (3), (-3)$$

$$HB^{\cdot} + HB^{\cdot} \rightleftharpoons B + H_2B \quad (4), (-4)$$

$$HA^{\cdot} + HB^{\cdot} \rightleftharpoons H_2B + A \quad (5), (-5)$$

$$HA^{\cdot} + HA^{\cdot} \rightleftharpoons H_2A + A \quad (6), (-6)$$

Table 1. Experimental[a] rate constants (*k*) for elementary steps of reversible chain reaction of *N*-phenyl-1,4-benzoquinoneimine (B) with 2,5-dichlorohydroquinone (H_2A) resulting in 4-hydroxydiphenylamine (H_2B) and 2,5-dichloroquinone (A) in chlorobenzene at $T = 298$ K, $K_{eq} = 0.31$

Step		k/L mol^{-1} s^{-1}		
		Direct reaction[17] $B + H_2A$	Reverse reaction[18] $A + H_2B$	Used in the present study for mathematical modeling
$B + H_2A \rightleftarrows HA^{\cdot} + HB^{\cdot}$	(1), (–1)	$k_1 = (3.5\pm1)\cdot10^{-4}$	—[b]	$k_1 = 3.5\cdot10^{-4}$
		$k_{-1} = 8\cdot10^8$	$k_{-1} = 8\cdot10^8$	$k_{-1} = 8\cdot10^8$
$B + HA^{\cdot} \rightleftarrows HB^{\cdot} + A$	(2), (–2)	$k_2 = (1.8\pm0.7)\cdot10^6$	$k_2 = (3.1\pm0.2)\cdot10^6$	$k_2 = 2.8\cdot10^6$
		$k_{-2} = (6\pm2.5)\cdot10^5$	$k_{-2} = (6.3\pm1.3)\cdot10^5$	$k_{-2} = 4.8\cdot10^5$
$HB^{\cdot} + H_2A \rightleftarrows H_2B + HA^{\cdot}$	(3), (–3)	$k_3 = (2.4\pm0.6)\cdot10^5$	$k_3 = (3.4\pm0.8)\cdot10^5$	$k_3 = 1.8\cdot10^5$
		$k_{-3} = (2.3\pm0.3)\cdot10^6$	$k_{-3} = (2.7\pm1)\cdot10^6$	$k_{-3} = 3.3\cdot10^6$
$HB^{\cdot} + HB^{\cdot} \rightleftarrows B + H_2B$	(4), (–4)	$k_4 = 8\cdot10^8$	$k_4 = 8\cdot10^8$	$k_4 = 8\cdot10^8$
		$k_{-4} = 6.4\cdot10^{-3}$ [c]	$k_{-4} = 6.4\cdot10^{-3}$ [c]	$k_{-4} = 6.4\cdot10^{-3}$ [c]
$HA^{\cdot} + HB^{\cdot} \rightleftarrows A + H_2B$	(5), (–5)	—[d]	$k_{-5} = (1.5\pm0.5)\cdot10^{-3}$	$k_{-5} = 1.13\cdot10^{-3}$
		$k_5 = 8\cdot10^8$	$k_5 = 8\cdot10^8$	$k_5 = 8\cdot10^8$
$HA^{\cdot} + HA^{\cdot} \rightleftarrows H_2A + A$	(6), (–6)	$k_6 = 8\cdot10^8$	$k_6 = 8\cdot10^8$	$k_6 = 8\cdot10^8$
		$k_{-6} = (0.8\pm0.4)\cdot10^{-4}$	$k_{-6} = (2.2\pm0.9)\cdot10^{-4}$	$k_{-6} = 6\cdot10^{-5}$

[a] Assuming that $k_{-1} = k_4 = k_5 = k_6$.

[b] The rate constant k_1 cannot be determined by studying the kinetics of the reverse reaction.

[c] See Ref. 19.

[d] The rate constant k_{-5} cannot be determined by studying the kinetics of the direct reaction.

equal to each other and the concentrations of the non-radical substances and semiquinone radicals $HA^\cdot$ and $HB^\cdot$ reach their steady-state values. This is an equilibrium state for each elementary step and for the overall reaction.[1,20]

Non-chain reactions described by the stoichiometric equation (s), (–s). Let us consider two non-chain mechanisms (*a*) and (*b*) representing fragments of the kinetic schemes of reversible chain reactions (see below).

Mechanism (*a*). By combining the chain initiation and chain termination steps (–1), (1) and (5), (–5), respectively (see Scheme 2) one gets mechanism (*a*) shown in Scheme 3.

Scheme 3*

$$B + H_2A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \boxed{HA^\cdot + HB^\cdot} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H_2B + A$$

Mechanism (*a*) is a detailed analog of the (s), (–s) mechanism. It includes a radical pool containing the $HA^\cdot$ and $HB^\cdot$ radicals existing in equilibrium with the "external space" of non-radical substances (initial reactants and products). Following reactions (1) and (–5), the radical pool is filled with the $HA^\cdot$ and $HB^\cdot$ radicals that are consumed in the reversible reactions (–1) and (5). Unlike the (s), (–s) mechanism, the rate constants for the reactions in mechanism (*a*) have a clear physical meaning and the experimental equilibrium constant $(K_{eq})_a$ is related to the equilibrium constants of the steps (–1), (1) and (–5), (5) as follows:

$$(K_{eq})_a = K_{eq} = \frac{[H_2B][A]}{[B][H_2A]} = \frac{K_1}{K_{-5}} = K_1K_5. \qquad (2)$$

Let us calculate the radical concentrations for mechanism (*a*). Consider the equation

$$\frac{d([HA^\cdot]_a + [HB^\cdot]_a)}{dt} = I_a + V_a = 0, \qquad (3)$$

where

$$I_a = k_1[B][H_2A] - k_{-1}[HA^\cdot]_a[HB^\cdot]_a = 0,$$

$$V_a = k_{-5}[A][H_2B] - k_5[HA^\cdot]_a[HB^\cdot]_a = 0.$$

Each of the four elementary reactions in mechanism (*a*) involves simultaneous production or loss of equivalent amounts of both radicals, $HA^\cdot$ and $HB^\cdot$, and the radical concentrations cannot be redistributed (due to, *e.g.*, reactions with non-radical products). It follows that the concentrations of the radicals $HA^\cdot$ and $HB^\cdot$ in mechanism (*a*) are equal to

$$[HA^\cdot]_a = [HB^\cdot]_a = (K_1[B][H_2A])^{1/2} = \\ = (K_{-5}[H_2B][A])^{1/2}. \qquad (4)$$

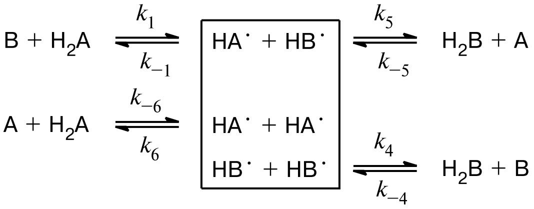
Equality (2) is consistent with the experimental data for more complex reversible chain reactions of quinoneimines with hydroquinones (see Table 1). This result is not surprising; it can be obtained by deriving from Scheme 2 relations between the equilibrium constant of the complex reversible reaction and the equilibrium constants of particular elementary steps by their summation.[21,22] For instance, summation of the steps (–1), (1) and (–5), (5) gives the stoichiometric equation for the mechanism (s), (–s) from which Eq. (2) follows. Using this approach, one can show that the equality

$$K_{eq} = K_1K_5 \qquad (5)$$

holds for all reactions described by the equations (s), (–s).

Mechanism (*b*) constructed by augmenting the mechanism (*a*) with two reversible reactions (4), (–4) and (6), (–6) is shown in Scheme 4.

Scheme 4



Mechanism (*b*) corresponds to the stoichiometric equation (s), (–s), is part of the mechanism of reversible chain reactions of quinoneimines with hydroquinones, and includes all steps of production and loss of the $HA^\cdot$ and $HB^\cdot$ radicals.

The concentrations of the $[HA^\cdot]_b$ and $[HB^\cdot]_b$ radicals in mechanism (*b*) can be calculated using the equation for their steady-state total concentration:

$$\frac{d([HA^\cdot]_b + [HB^\cdot]_b)}{dt} = I_b + IV_b + V_b + VI_b = 0, \qquad (6)$$

where

$$I_b = k_{1b}[B][H_2A] - k_{-1b}[HA^\cdot]_b[HB^\cdot]_b,$$

$$IV_b = k_{-4b}[B][H_2B] - k_{4b}[HB^\cdot]_b^2,$$

$$V_b = k_{-5b}[A][H_2B] - k_{5b}[HA^\cdot]_b[HB^\cdot]_b,$$

$$VI_b = k_{-6b}[A][H_2A] - k_{6b}[HA^\cdot]_b^2.$$

Using the principle of detailed equilibrium,[20,22,23] from VI_b and IV_b one gets the expressions for $[HA^\cdot]_b$ and $[HB^\cdot]_b$

$$[HA^\cdot]_b = (K_{-6}[A][H_2A])^{1/2}, \qquad (7)$$

$$[HB^\cdot]_b = (K_{-4}[B][H_2B])^{1/2}. \qquad (8)$$

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* From this point on, the radical pool in the schemes is given by solid lines.

Now we will find relations between the equilibrium constants. Substituting expressions (7) and (8) into I_b, one gets

$$k_1[\mathrm{B}][\mathrm{H_2A}] = k_{-1}[\mathrm{HA}^{\cdot}]_b[\mathrm{HB}^{\cdot}]_b = $$
$$= k_{-1}(K_{-4}K_{-6}[\mathrm{A}][\mathrm{H_2A}][\mathrm{B}][\mathrm{H_2B}])^{1/2},$$

from which it follows

$$K_{\mathrm{eq}} = K_1{}^2K_4K_6. \qquad (9)$$

Substitution of relationships (7) and (8) into V_b gives the equality

$$K_{\mathrm{eq}} = K_5{}^2K_{-4}K_{-6}. \qquad (10)$$

Equation (10) can also be obtained by substituting expression (9) into relation (2) for the mechanism (*a*). Also, both relations (9) and (10) can be obtained by summation of elementary steps (see above). Thus, by summing the doubled step (1) and the steps (4) and (6) (see Scheme 2) we get the stoichiometric equation (s), (–s) from which equality (9) follows.

Dividing expression (9) by relation (10), one also gets

$$K_1K_4K_{-5}K_6 = 1. \qquad (11)$$

Finally, having multiplied Eq. (9) by Eq. (10), we assure that relation (2) also holds for mechanism (*b*)

$$(K_{\mathrm{eq}})_b = K_{\mathrm{eq}} = \frac{[\mathrm{H_2B}][\mathrm{A}]}{[\mathrm{B}][\mathrm{H_2A}]} = \frac{K_1}{K_{-5}} = K_1K_5. \qquad (2')$$

All relations derived for mechanism (*b*) agree with the experimental data (see Table 1).

Mechanism of reversible chain reactions of quinoneimines with hydroquinones, or mechanism (*c*). Augmentation of mechanism (*b*) with two reversible chain propagation steps (2), (–2) and (3), (–3) (see Scheme 2) gives the mechanism of reversible chain reactions of quinoneimines with hydroquinones. For clarity, it can also be represented as follows (Scheme 5).

Mechanism (*c*) corresponds to the stoichiometric equation (s), (–s) and describes both the equilibrium and the reaction kinetics.

Augmentation with the fast steps (2), (–2) and (3), (–3) does not violate the equilibrium state of all reversible steps in mechanism (*b*) and has no effect on the concentrations of non-radical substances in this mechanism (because $K_{\mathrm{eq}(b)} = K_{\mathrm{eq}(c)} = K_{\mathrm{eq}}$) as well as radicals, *i.e.*

$$[\mathrm{HA}^{\cdot}]_b = [\mathrm{HA}^{\cdot}]_c,\ [\mathrm{HB}^{\cdot}]_b = [\mathrm{HB}^{\cdot}]_c. \qquad (12)$$

It follows that all equalities derived for the non-chain mechanism (*b*) also hold for mechanism (*c*). Also, some additional relations are valid for mechanism (*c*); they can be derived using the equations for the equilibrium of steps (2), (–2) and (3), (–3)

$$k_2[\mathrm{B}][\mathrm{HA}^{\cdot}]_c - k_{-2}[\mathrm{A}][\mathrm{HB}^{\cdot}]_c = 0, \qquad (13)$$

$$k_3[\mathrm{H_2A}][\mathrm{HB}^{\cdot}]_c - k_{-3}[\mathrm{H_2B}][\mathrm{HA}^{\cdot}]_c = 0. \qquad (14)$$

Substituting the expressions for $[\mathrm{HA}^{\cdot}]_b$ and $[\mathrm{HB}^{\cdot}]_b$ from Eqs (7) and (8) into Eqs (13) and (14) (taking into account relation (12)), one gets

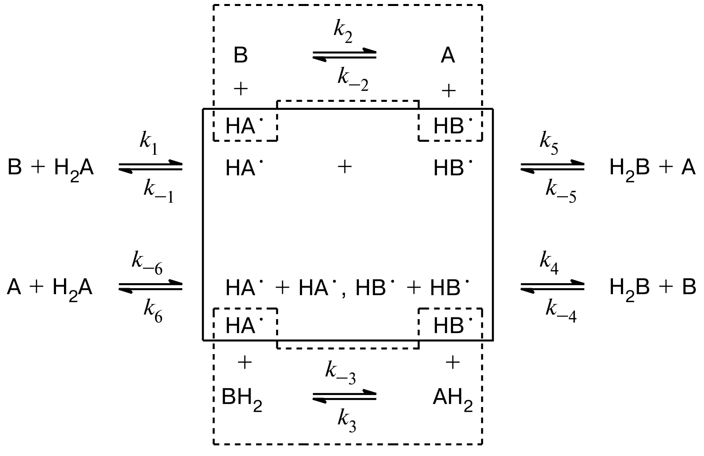
$$K_{\mathrm{eq}} = K_2{}^2K_4K_{-6}, \qquad (15)$$

$$K_{\mathrm{eq}} = K_3{}^2K_{-4}K_6. \qquad (16)$$

Taking into account expressions (9) and (10), from Eqs (15) and (16), one gets the following additional relations:

$$K_{\mathrm{eq}} = K_1K_2K_4 = K_2K_5K_{-6} = K_1K_3K_6 = K_3K_5K_{-4}, \qquad (17)$$

Scheme 5*



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* From this point on, dashed lines denote the chain propagation reactions resulting in the change of one type of radicals by some other type of radicals. Such a change involves the "external space" of non-radical substances.

and the equations relating the equilibrium constants for chain propagation K_2 and K_3 to the equilibrium constants of the chain initiation and chain termination steps

$$K_2 = K_1K_6 = K_5K_{-4}, \quad (18)$$

$$K_3 = K_1K_4 = K_5K_{-6}. \quad (18')$$

Having multiplied expression (15) by (16), one gets the equation

$$K_{eq} = K_2K_3, \quad (19)$$

which can be combined with expression (5) and written as an important relation

$$K_{eq} = K_1K_5 = K_2K_3. \quad (20)$$

Finally, from (18) and (19) one finds that

$$K_{eq} = K_1{}^2K_4K_6 = K_5{}^2K_{-4}K_{-6} = K_1K_5. \quad (21)$$

All the equalities derived are consistent with the data listed in Table 1.

The relations derived allow the *k* values to be refined (see Table 1). Using the "refined" *k* values, we calculated the reactant concentrations and the rates of elementary steps in the equilibrium state for the reaction of 2,5-dichlorohydroquinone with *N*-phenyl-1,4-benzoquinonemonoimine, which proceeds by the mechanism (*c*). For comparison, we also obtained independent estimates of the equilibrium concentrations by mathematical modeling of the reaction kinetics using the "refined" *k* values from Table 1. For certainty, we considered a case where $[B]_0 = 4 \cdot 10^{-4}$ mol L^{-1}, $[H_2A]_0 = 2 \cdot 10^{-4}$ mol L^{-1}, and $[H_2B]_0 = [A]_0 = 0$. The results obtained are shown in Fig. 1 and listed in Table 2.

As follows from the data of Table 2, analytical calculations and mathematical modeling give almost identical results (within the accuracy of the error in the determination of the *k* values). Using these results and the "refined" *k* values (see Table 1), we calculated the rates of elementary steps of the reaction in the equilibrium state (Table 3).

Table 2. Equilibrium concentrations of reaction components according to the results of calculations and mathematical modeling

Substance	Equilibrium concentrations/mol L^{-1}	
	Calculations	Mathematical modeling[a]
B	$3.02 \cdot 10^{-4}$ [b]	$3.01 \cdot 10^{-4}$
H_2A	$1.02 \cdot 10^{-4}$ [b]	$1.01 \cdot 10^{-4}$
H_2B	$9.78 \cdot 10^{-5}$ [b]	$9.86 \cdot 10^{-5}$
A	$9.78 \cdot 10^{-5}$ [b]	$9.86 \cdot 10^{-5}$
$HA^{\cdot}$	$2.74 \cdot 10^{-11}$ [c]	$2.74 \cdot 10^{-11}$
$HB^{\cdot}$	$4.86 \cdot 10^{-10}$ [d]	$4.88 \cdot 10^{-10}$

[a] Concentrations at $t = 10^8$ s.

[b] Calculated using expression (1).

[c] Calculated using expression (5).

[d] Calculated using expression (6).

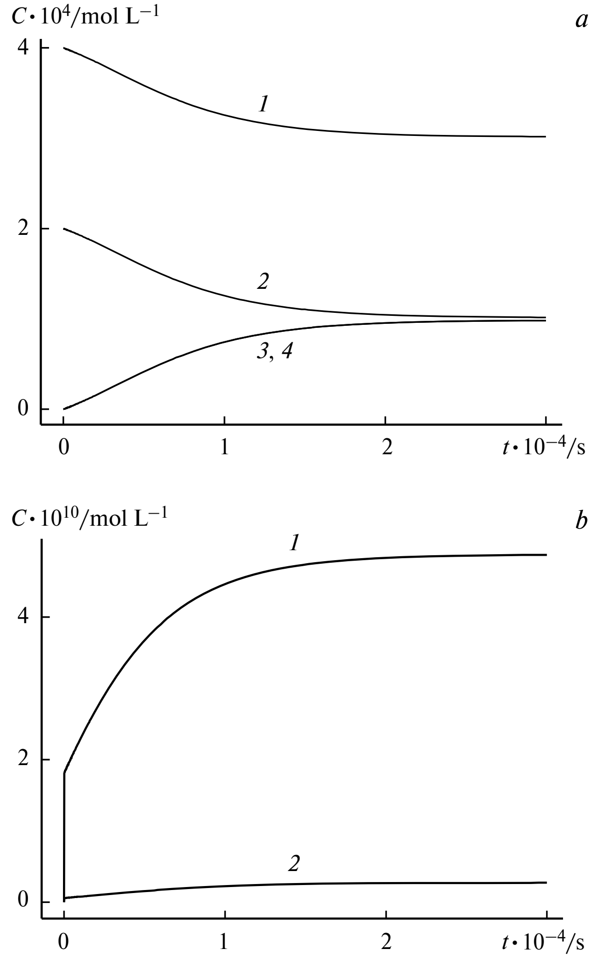


Fig. 1. Calculated kinetic curves for a reversible chain reaction proceeding by mechanism (*c*): (*a*) — initial reactants and products B (*1*), H_2A (*2*), H_2B (*3*), A (*4*); (*b*) radicals $HB^{\cdot}$ (*1*) and $HA^{\cdot}$ (*2*). $[B]_0 = 4 \cdot 10^{-4}$ mol L^{-1}, $[H_2A]_0 = 2 \cdot 10^{-4}$ mol L^{-1}.

From the data of Table 3 it follows that the rates of each step in the direct and reverse directions are equal within the limits of experimental error, but the rates of different steps differ by almost five orders of magnitude.

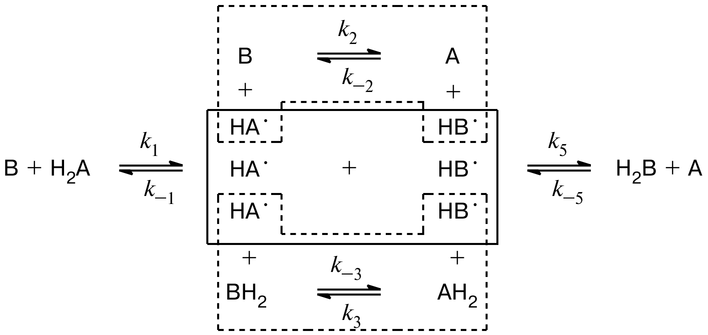
"Simplified mechanisms" of reversible chain reactions of quinoneimines with hydroquinones, or mechanisms (*d*) and (*e*). Augmentation of mechanism (*a*) with the chain propagation steps (2), (−2) and (3), (−3) gives a new chain mechanism (*d*) which corresponds to the stoichiometric equation (s), (−s) and describes a new reversible chain reaction of B with H_2A yielding H_2B and A.

This mechanism can also be constructed by excluding steps (4), (−4) and (6), (−6) from the reaction mechanism (*c*) describing the reaction of quinoneimines with

Table 3. Rates of elementary steps in the equilibrium state

Step		Rate at dynamic equilibrium /mol L^{-1} s^{-1}	
		Direct reaction	Reverse reaction
$B + H_2A \rightleftarrows HA^\bullet + HB^\bullet$	(1), (–1)	$1.06 \cdot 10^{-11}$	$1.07 \cdot 10^{-11}$
$B + HA^\bullet \rightleftarrows HB^\bullet + A$	(2), (–2)	$2.31 \cdot 10^{-8}$	$2.31 \cdot 10^{-8}$
$HB^\bullet + H_2A \rightleftarrows H_2B + HA^\bullet$	(3), (–3)	$8.87 \cdot 10^{-9}$	$8.92 \cdot 10^{-9}$
$HB^\bullet + HB^\bullet \rightleftarrows B + H_2B$	(4), (–4)	$1.91 \cdot 10^{-10}$	$1.90 \cdot 10^{-10}$
$HA^\bullet + HB^\bullet \rightleftarrows A + H_2B$	(5), (–5)	$1.07 \cdot 10^{-11}$	$1.10 \cdot 10^{-11}$
$HA^\bullet + HA^\bullet \rightleftarrows H_2A + A$	(6), (–6)	$6.01 \cdot 10^{-13}$	$5.98 \cdot 10^{-13}$

Scheme 6



hydroquinones. Similar to mechanism (*c*), the equilibrium state in mechanism (*d*) can be attained in a chain manner from the initial reactants B and H_2A, as well as from the products H_2B and A. Also, the direct and reverse reactions are accelerated in the presence of initiators.

Prior to considering the chain mechanism (*d*), it is necessary to compare the concentrations of radicals in the non-chain mechanisms (*a*) and (*b*).

Equalities (4) for $[HA^\bullet]_a$ and $[HB^\bullet]_a$ differ from equalities (7) and (8) for $[HA^\bullet]_b$ and $[HB^\bullet]_b$, respectively. This means that the concentrations of $HA^\bullet$ and $HB^\bullet$ radicals in mechanisms (*a*) and (*b*) are different. Now we will show that in mechanism (*b*), the concentration of one of the two radicals ($HB^\bullet$ or $HA^\bullet$) is higher while that of the other radical is lower than their concentrations in mechanism (*a*). The total concentration of radicals, $[HA^\bullet]_b + [HB^\bullet]_b$, in mechanism (*b*) is usually higher than the total concentration of radicals in mechanism (*a*), but the product of the radical concentrations, $[HA^\bullet]_a[HB^\bullet]_a$, in mechanism (*a*) equals the product of the radical concentration in mechanism (*b*).

To prove this, let us calculate the ratio of the radical concentrations in mechanisms (*b*) and (*a*) using expressions (4), (7), (8), and (11):

$$\frac{[HA^\bullet]_b}{[HA^\bullet]_a} = \left(K_{-6}K_5\frac{[H_2A]}{[H_2B]}\right)^{1/2} = \left(K_{-6}K_5\frac{1}{K_{eq}}\frac{[A]}{[B]}\right)^{1/2} = \xi, \quad (22)$$

$$\frac{[HB^\bullet]_b}{[HB^\bullet]_a} = \left(K_{-4}K_{-1}\frac{[H_2B]}{[H_2A]}\right)^{1/2} = \left(K_{-4}K_{-1}K_{eq}\frac{[B]}{[A]}\right)^{1/2} = \xi^{-1}. \quad (23)$$

Taking into account the equalities (22) and (23), the sum $[AH^\bullet]_b + [BH^\bullet]_b$ is given by

$$[AH^\bullet]_b + [BH^\bullet]_b = [AH^\bullet]_a\xi + [BH^\bullet]_a\xi^{-1} = [AH^\bullet]_a(\xi + \xi^{-1}) = [BH^\bullet]_a(\xi + \xi^{-1}). \quad (24)$$

At $\xi > 0$, the function $y = \xi + \xi^{-1}$ is positive and has a minimum value $y = 2$ at $\xi = 1$. Since, generally, one has $\xi \neq 1$, then one gets $y > 2$ and

$$\frac{[HA^\bullet]_b + [HB^\bullet]_b}{[HA^\bullet]_a + [HB^\bullet]_a} > 1, \quad (25)$$

i.e., the total concentration of radicals, $[HA^\bullet] + [HB^\bullet]$, in mechanism (*b*) is higher than the total concentration of radicals in mechanism (*a*).

Also, from expressions (22) and (23) it follows that for mechanism (*b*), the concentration of $AH^\bullet$ radicals is by a factor of ξ higher while that of $BH^\bullet$ radicals is by a factor of ξ lower than the corresponding values for mechanism (*a*). As a consequence, the product of the radical concentrations in mechanism (*b*) equals the product of the radical concentrations in mechanism (*a*):

$$[\mathrm{HA}^{\bullet}]_b[\mathrm{HB}^{\bullet}]_b = [\mathrm{HA}^{\bullet}]_a[\mathrm{HB}^{\bullet}]_a, \qquad (26)$$

which should be proved.

Figure 2 presents the results of mathematical modeling of the kinetics of non-chain reversible reactions proceeding by the mechanisms (*a*) and (*b*). As can be seen, mathematical modeling and our analysis of mechanisms (*a*) and (*b*) lead to the same results. Mathematical modeling was carried out using the "refined" *k* values (see Table 1).

Figures 1 and 2 allow one to compare two reactions, one proceeding by the chain mechanism (*c*) (see Fig. 1) and the other following the non-chain mechanism (*b*) that precedes the mechanism (*c*) (see Fig. 2). As can be seen, in the equilibrium state, the concentrations of radicals and non-radical substances in the chain mechanism (*c*) are equal to the concentrations of the corresponding radical and non-radical substances in the non-chain mechanism (*b*). As follows from a comparison of the *X*-axis scales in Figs 1 and 2, the chain reaction (*c*) is much faster than the non-chain reaction (*b*).

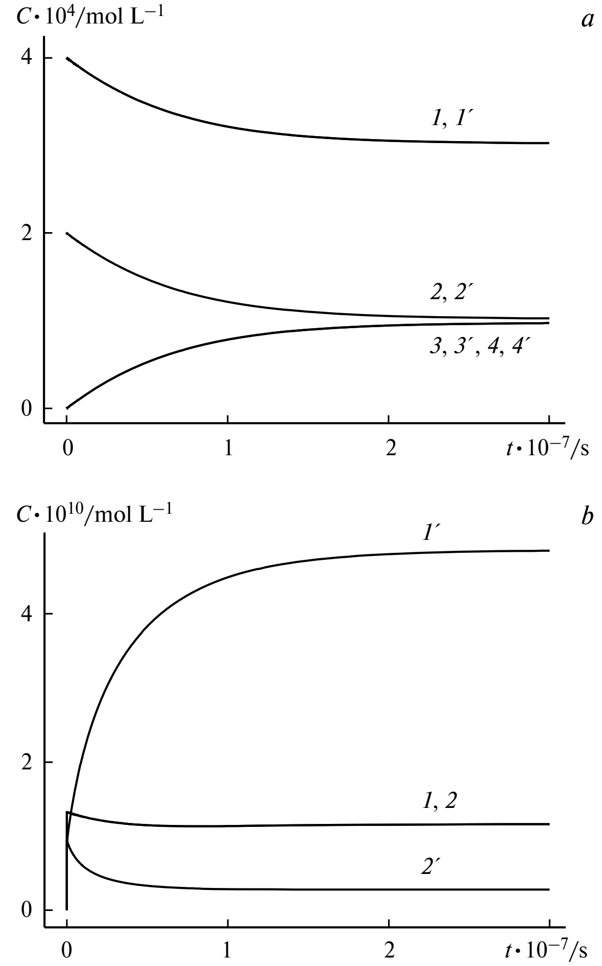


Fig. 2. Calculated kinetic curves for non-chain reversible reactions proceeding by the mechanism (*a*) (*1—4*) and mechanism (*b*) (*1′—4′*): (*a*) — initial reactants and products B (*1, 1′*), H_2A (*2, 2′*), H_2B (*3, 3′*), A (*4, 4′*); (*b*) — radicals $HB^{\bullet}$ (*1, 1′*), $HA^{\bullet}$ (*2, 2′*). $[B]_0 = 4 \cdot 10^{-4}$, $[H_2A]_0 = 2 \cdot 10^{-4}$ mol L^{-1}.

Next, we will calculate the equilibrium concentrations of radicals $[\mathrm{HA}^{\bullet}]_d$ and $[\mathrm{HB}^{\bullet}]_d$ and compare them with the concentration of radicals in the non-chain predecessor mechanism (*a*). Note that the radical concentrations in the chain mechanism (*c*) are equal to the concentrations of the corresponding radicals for the non-chain mechanism (*b*) which is a part of the chain mechanism (*c*) (see equalities (12)).

When calculating $[\mathrm{HA}^{\bullet}]_d$ and $[\mathrm{HB}^{\bullet}]_d$, first, we take into account the equations for the equilibrium steps (2) and (3), according to which the equilibrium radical concentrations in the chain reactions are related as follows:

$$[\mathrm{HB}^{\bullet}] = K_2\frac{[\mathrm{B}]}{[\mathrm{A}]}[\mathrm{HA}^{\bullet}] = K_{-3}\frac{[\mathrm{H_2B}]}{[\mathrm{H_2A}]}[\mathrm{HA}^{\bullet}]. \qquad (27)$$

Second, based on equalities (26) and (4), we can write

$$[\mathrm{HA}^{\bullet}]_d[\mathrm{HB}^{\bullet}]_d = [\mathrm{HA}^{\bullet}]_a[\mathrm{HB}^{\bullet}]_a = K_1[\mathrm{B}][\mathrm{H_2A}]. \qquad (28)$$

From Eqs (27) and (28) one gets

$$[\mathrm{HA}^{\bullet}]_d = \left(\frac{K_1}{K_2}[\mathrm{A}][\mathrm{H_2A}]\right)^{1/2}$$

and

$$[\mathrm{HB}^{\bullet}]_d = [\mathrm{B}]\left(K_1K_2\frac{[\mathrm{H_2A}]}{[\mathrm{A}]}\right)^{1/2}. \qquad (29)$$

Having compared expressions (29) for $[\mathrm{HA}^{\bullet}]_d$ and $[\mathrm{HB}^{\bullet}]_d$ with equalities (7) and (8) and taking into account relations (18) and (18′), we can conclude that the radical concentrations in mechanism (*d*) differ from the concentrations of the same radicals in the non-chain predecessor mechanism (*a*) but are equal to the radical concentrations in mechanisms (*c*) and (*b*). This is in complete agreement with the results of mathematical modeling of the reaction kinetics for mechanism (*d*) (Fig. 3).

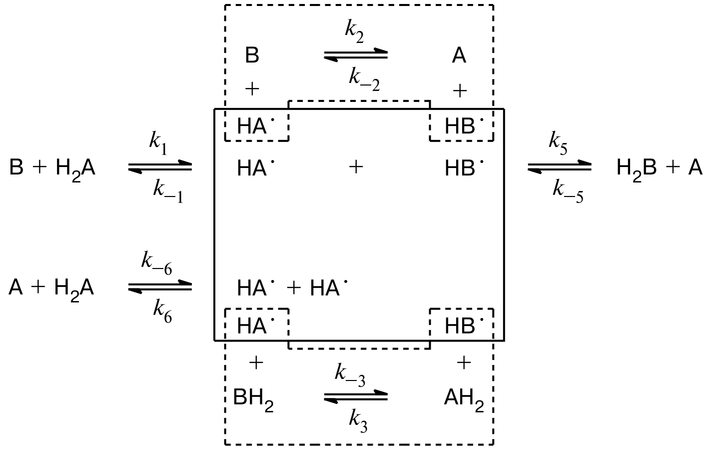
For mechanism (*d*), relations (5) and (19) are also valid. They relate the equilibrium constant of the overall reaction to the products of the equilibrium constants of the chain initiation—chain termination and chain propagation stages.

Let us now consider mechanism (*e*) (Scheme 7). In contrast to mechanism (*c*), this mechanism does not include one reversible chain initiation—chain termination reaction involving only one kind of radicals. It is assumed that reactions (4), (–4) do not occur.

As mentioned above for mechanism (*e*), the concentrations of non-radical substances are equal to the concentrations of these substances in all previously studied mechanisms; also, the equilibrium radical concentration $[\mathrm{HA}^{\bullet}]_e$ can be calculated as follows:

$$[\mathrm{HA}^{\bullet}]_e = (K_{-6}[\mathrm{A}][\mathrm{H_2A}])^{1/2}. \qquad (30)$$

Scheme 7



Having compared relation (30) with the expressions for the $HA^{\cdot}$ radical concentration in mechanisms (*b*), (*c*) and (*d*), one gets

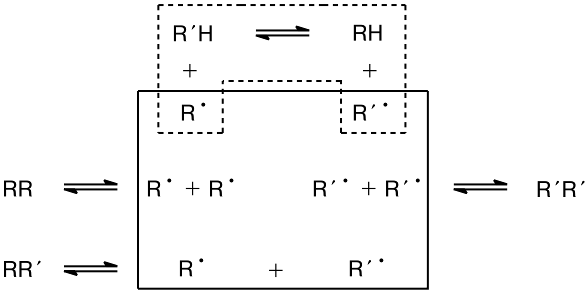
$$[HA^{\cdot}]_e = [HA^{\cdot}]_b = [HA^{\cdot}]_c = [HA^{\cdot}]_d. \qquad (31)$$

Taking into account the fact that the radical concentrations are interrelated by expression (27), one gets that

$$[HB^{\cdot}]_e = [HB^{\cdot}]_b = [HB^{\cdot}]_c = [HB^{\cdot}]_d. \qquad (32)$$

There is a number of real liquid-phase reactions proceeding by the chain mechanism (*d*) or by a similar mechanism. For instance, one may consider a system containing hexaphenylethane Ph_3CCPh_3 (RR), which readily dissociates into radicals $R^{\cdot}$, and deuterated triphenylmethane $(C_6H_4D)_3CH$ (R´H). At a certain ratio of reactant concentrations, one can create a situation where the total initiation rate will be lower than the rate of chain propagation in the hydrogen abstraction steps. In these cases, a reversible chain reaction between RR and R´H resulting in RH, R´R, and R´R´ will proceed by mechanism (*f*) in the system (Scheme 8).

Scheme 8



The mechanism of reversible chain reactions with one reversible chain termination step, or mechanism (*g*). Exclusion of one chain initiation—chain termination step (1), (–1) or (5), (–5) in mechanism (*d*) gives a chain mechanism

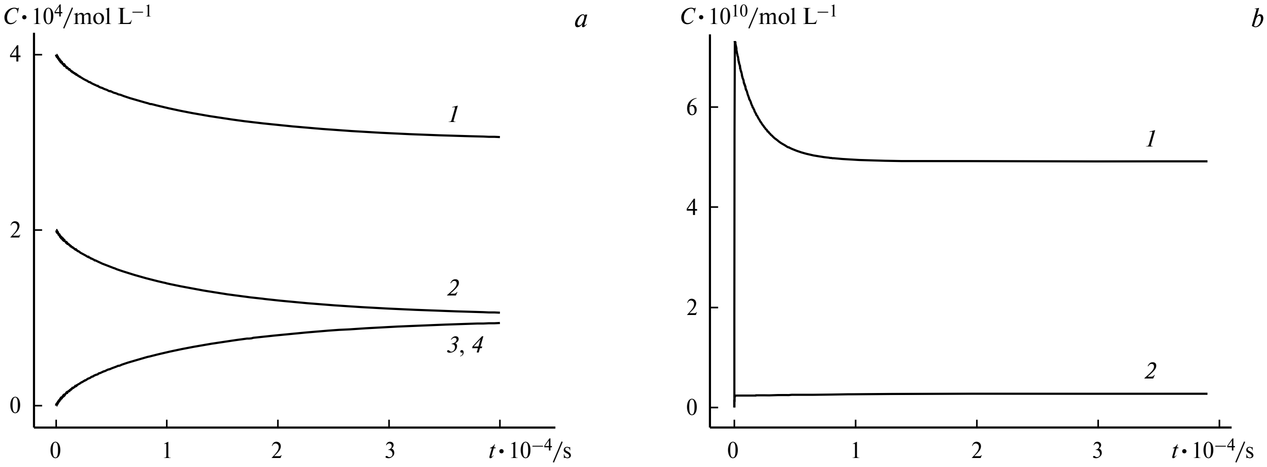
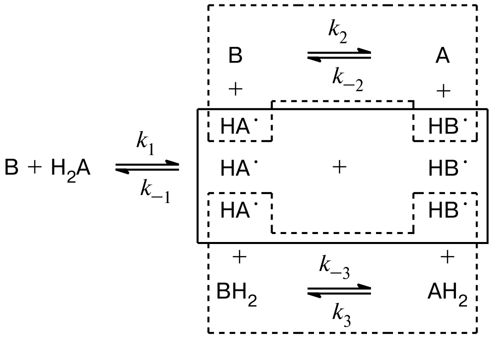


Fig. 3. Calculated kinetic curves for reversible chain reaction proceeding by mechanism (*d*): (*a*) – initial reactants and products B (*1*), H_2A (*2*), H_2B (*3*), A (*4*); (*b*) — radicals $HB^{\cdot}$ (*1*) and $HA^{\cdot}$ (*2*). $[B]_0 = 4 \cdot 10^{-4}$, $[H_2A]_0 = 2 \cdot 10^{-4}$ mol L^{-1}.

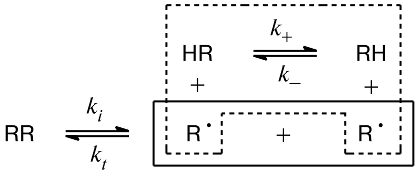
(*g*) which describes yet another reversible chain reaction of B with H_2A resulting in H_2B and A. This reaction is also described by the stoichiometric equation (s), (–s). For clarity, we exclude steps (5), (–5). Mechanism (*g*) includes only one chain initiation step (1), one chain termination step (–1), and two chain propagation steps (2), (3) and (–2), (–3) for the direct and reverse chain reactions, respectively (Scheme 9).

Scheme 9



As in the case of mechanisms (*c*)—(*e*), the chain reaction proceeding by the mechanism (*g*) accelerates in the presence of initiator. But unlike those mechanisms, the equilibrium state in mechanism (*g*) can be reached only starting from the initial reactants B and H_2A. For mechanism (*g*), Eq. (19) holds, which relates the equilibrium constant of the overall reaction to the products of the equilibrium constants of the chain propagation steps (2), (–2) and (3), (–3). The product of the radical concentrations, $[HA^\cdot][HB^\cdot]$, is the same for mechanism (*g*) and all mechanisms considered above. In particular, exclusion of three (out of four) reversible chain initiation—chain termination reactions (4), (–4), (5), (–5) and (6), (–6) from mechanism (*c*) gives the same equilibrium concentrations of non-radical substances and radicals in mechanism (*g*) as in mechanism (*c*).

Scheme 10



Reversible chain reactions with one chain initiation—chain termination step and, often, with one reversible chain propagation step are not rare to occur. For instance, a reversible chain reaction can proceed by mechanism (*h*) in solutions of a radical dimer RR (*e.g.*, hexaphenylethane Ph_3CCPh_3) and its hydrogenated form RH (*e.g.*, triphenylmethane Ph_3CH) under particular conditions (Scheme 10).

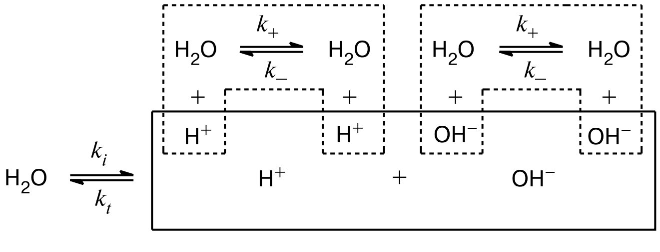
If radical dimers of phenoxyl radicals $(ArO^\cdot)_2$ are used instead of RR and the corresponding phenols ArOH are used as RH, one gets a system in which a reversible chain reaction involving oxygen- rather than carbon-centered radicals may proceed. Some other examples are available.

The difference between mechanisms (*f*) and (*h*) is as follows: in the former case, the elementary steps proceed involving distinguishable radicals $R^\cdot$ and $R'^\cdot$, whereas in the latter case, all reactions proceed involving one kind of radicals $R^\cdot$. Reversible chain reactions in which the chain propagation steps are the H-transfer reactions between two indistinguishable radicals $R^\cdot$ ($R^\cdot + RH \rightleftarrows RH + R^\cdot$) proceed from the very beginning in equilibrium with the corresponding reverse chain reactions, *i.e.*, for the equilibrium constants of these reactions one has $K_{eq} = 1$. These reactions show no visible transformations, but they do occur in chemical systems and are used to analyze, *e.g.*, the mechanism of relay race transfer of free valence.[24]

There are chain reactions carried out using charged particles (ions) rather than atoms or free radicals as the chain carriers (see, *e.g.*, Ref. 25). Some of them are reversible, *e.g.*, a reversible chain reaction between light water H_2O and heavy water D_2O.[26] Also, a reversible chain reaction proceed by the mechanism (*i*) in H_2O (Scheme 11).

Mechanism (*i*) includes two independent cycles comprising the chain propagation steps involving H^+ and HO^- ions and one chain initiation—chain termination step common to two chain reactions. Initiation occurs in the self-dissociation step of water to H^+ and HO^- ions (ion hydration is ignored) while chain termination occurs

Scheme 11



through recombination of H^+ with HO^-. Reversible chain propagation reactions in mechanism (*i*)

$$H^+ + H_2O \rightleftharpoons H_2O + H^+,$$

$$HO^- + H_2O \rightleftharpoons H_2O + HO^-$$

do occur and provide an explanation for abnormally high mobility of HO^- and especially H^+ ions in water.[21]

Summing up, in the present study we considered the equilibria in some real and hypothetical reversible chain reactions. For all mechanisms, the equilibrium concentrations of radicals and non-radical reaction participants are calculated; for some mechanisms, the results of analysis were compared with the results obtained by mathematical modeling. Relations were derived relating the equilibrium constants of elementary steps to one another and to the equilibrium constant of the overall chain reaction. Examples are provided that reversible chain reactions are not rare to occur.

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References

1. S. W. Benson, *The Foundations of Chemical Kinetics*, McGrow-Hill, New York, 1960.
2. S. W. Benson, *Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters*, John Wiley and Sons, New York, 1968, 223 pp.
3. N. N. Semenov, *O Nekotorykh problemakh khimicheskoy kinetiki i reaktsionnoy sposobnosti* [*Some Problems in Chemical Kinetics and Reactivity*], Selected Works in 4 Vols, Vol. **3**, Nauka, Moscow, 2005, 499 pp. (in Russian).
4. S. H. Bauer, E. Ossa, *J. Chem. Phys.*, 1966, **45**, 434.
5. A. Burcat, A. Lifshits, *J. Chem. Phys.*, 1967, **47**, 3079.
6. D. Lewis, S. H. Bauer, *J. Am. Chem. Soc.*, 1968, **90**, 5390.
7. R. P. N. Veregin, M. K. Georges, P. M. Kazmaier, G. K. Hamer, *Polym. Mater. Sci. Eng.*, 1993, **68**, 8.
8. M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, G. K. Hamer, *Macromolecules*, 1993, **26**, 2987.
9. R. P. N. Veregin, M. K. Georges, P. M. Kazmaier, G. K. Hamer, *Macromolecules*, 1993, **26**, 5316.
10. V. T. Varlamov, *Dokl. Akad. Nauk*, 1993, **332**, 457 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1993, **332**].
11. V. T. Varlamov, *Kinet. Kataliz*, 2001, **42**, 836 [*Kinet. Catal.* (*Engl. Transl.*), 2001, **42**, 759].
12. G. V. Korolyov, A. P. Marchenko, *Usp. Khim.*, 2000, **69**, 447 [*Russ. Chem. Rev.* (*Engl. Transl.*), 2000, **69**, 409].
13. G. Moad, D. H. Solomon, *The Chemistry of Radical Polymerization*, Elsevier, London, 2005, 666 pp.
14. W. Braunecker, K. Matyjaszewski, *Prog. Polym. Sci.*, 2007, **32**, 93.
15. *Controlled/Living Radical Polymerization: Progress in ATRP*, *ACS Symposium Series*, vol. **1023**, Ed. K. Matyjaszewski, ACS Publ., Washington (DC), 2009, 423 pp.
16. *Controlled/Living Radical Polymerization: Progress in RAFT*, *DT*, *NMP and OMRP*, *ACS Symposium Series*, vol. **1024**, Ed. K. Matyjaszewski, ACS Publ., Washington (DC), 2009, 403.
17. A. V. Antonov, V. T. Varlamov, *Izv. Akad. Nauk. Ser. Khim*, 2007, 849 [*Russ. Chem. Bull.*, *Int. Ed.*, 2007, **56**, 883].
18. A. V. Antonov, V. T. Varlamov, *Zh. Fiz. Khim.*, 2007, **81**, 2186 [*Russ. J. Phys. Chem. A (Engl. Transl.)*, 2007, **81**, 1968].
19. V. T. Varlamov, *Dokl. Akad. Nauk*, 1994, **337**, 757 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1994, **337**].
20. V. N. Kondrat´ev, E. E. Nikitin, *Kinetika i mekhanizm gazofaznykh reaktsii* [*The Kinetics and Mechanisms of Gas-Phase Reactions*], Nauka, Moscow, 1974, 558 pp. (in Russian).
21. A. G. Stromberg, D. P. Semchenko, *Fizicheskaya khimiya* [*Physical Chemistry*], 2nd Ed., Vysshaya Shkola, Moscow, 1988, 496 pp. (in Russian).
22. S. L. Kiperman, *Osnovy khimicheskoi kinetiki v geterogennom katalize* [*The Foundations of Chemical Kinetics in Heterogeneous Catalysis*], Khimiya, Moscow, 1979, 352 pp. (in Russian).
23. I. A. Semiokhin, B. V. Strakhov, A. I. Osipov, *Kinetika khimicheskikh reaktsii* [*The Kinetics of Chemical Reactions*], Idz-vo. MGU, Moscow, 1995, 351 pp. (in Russian).
24. E. T. Denisov, *Usp. Khim.*, 1978, **47**, 1090 [*Russ. Chem. Rev.* (*Engl. Transl.*), 1978, **47**, 572].
25. A. P. Purmal´, *A*, *B*, *V... Khimicheskoi kinetiki* [*The ABC of Chemical Kinetics*], IKTs Akademkniga, Moscow, 2004, 277 pp. (in Russian).
26. V. T. Varlamov, *Butlerovskie Soobshcheniya*, 2010, **23**, 43 [*Butlerov Commun.* (*Engl. Transl.*), 2010, **23**].

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