Simulation of Initiated Nonbranched Chain Oxidation of Hydrogen: Oxygen as an Autoinhibitor

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Abstract—A simple kinetic equation describing nonmonotonic (with a maximum) dependence of the hydrogen peroxide and water formation rate on the oxygen concentration was derived by the quasi-steady-state treatment in terms of the nonbranched-chain free-radical mechanism of noncatalytic hydrogen oxidation involving the relatively low-reactive radical $HO_4^{\bullet}$, which inhibits the chain process. Possible nonchain pathways of the free-radical oxidation of hydrogen, the energetics of key radical-molecule reactions, and the routes of ozone decay from the energetics standpoint via the reaction with the $HO^{\bullet}$ radical in the upper atmosphere (including the addition yielding the $HO_4^{\bullet}$ radical, which can be an intermediate in the sequence of conversions of biologically hazardous UV radiation energy) were considered.
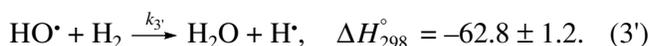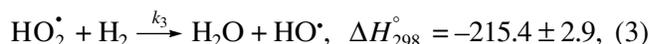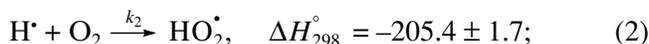
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The kinetics of inhibition for nonbranched-chain processes of addition of saturated free radicals to the C=C and C=O double bonds of alkene and formaldehyde molecules, respectively, by low-reactive free radicals that can experience delocalization of the unpaired *p*-electron was first considered in [1] and that for the addition of hydrocarbon free radicals was discussed in [2]. In this work, the dependence of the hydrogen peroxide formation rate on the oxygen concentration during the γ-radiolysis of water containing hydrogen and oxygen at initial concentrations of 7×10^{-4} and $(1–6) \times 10^{-5}$ mol dm^{-3}, respectively, at room temperature was mathematically simulated on the basis of the mechanism considered earlier [3] for the free-radical nonbranched-chain oxidation of hydrogen involving the $HO_4^{\bullet}$ intermediate species.

In the case of addition of hydrogen atoms to oxygen at moderate temperatures and pressures when the process does not pass to nonstationary critical regimes, the earlier analyzed competitive kinetics of free-radical addition [8] can be used for the explanation and kinetic substantiation of once considered experimental results [3] on the autoinhibition of hydrogen oxidation with oxygen with an increase in the oxygen concentration in the gas (Fig. 1) [5–7] and liquid (Fig. 2) [4] phases. The kinetics in question is based on a simplified scheme of nonbranched-chain reactions with the quadratic chain termination only without allowance for surface effects [6]. This scheme was proposed in [3] and involves the following elementary reactions at the chain evolution

stage (and the corresponding enthalpy changes ΔH°_{298} in the gas phase in kJ mol^{-1} [9, 10]).

Propagation:

$$H^{\bullet} + O_2 \xrightarrow{k_2} HO_2^{\bullet}, \quad \Delta H^{\circ}_{298} = -205.4 \pm 1.7; \quad (2)$$

$$HO_2^{\bullet} + H_2 \xrightarrow{k_3} H_2O + HO^{\bullet}, \quad \Delta H^{\circ}_{298} = -215.4 \pm 2.9, \quad (3)$$

$$(\text{or } H_2O_2 + H^{\bullet}), \quad \Delta H^{\circ}_{298} = 69.4 \pm 1.7;$$

$$HO^{\bullet} + H_2 \xrightarrow{k_{3'}} H_2O + H^{\bullet}, \quad \Delta H^{\circ}_{298} = -62.8 \pm 1.2. \quad (3')$$

Inhibition:

$$HO_2^{\bullet} + O_2 \xrightarrow{k_4} HO_4^{\bullet}, \quad \Delta H^{\circ}_{298} = 110.0 \pm 15.4^{1}. \quad (4)$$

Reactions (2) and (3) are consecutive; reactions (3) and (4) are parallel, or competing; and reactions (2) and (4), as well as the first variant of reaction (3) and reaction (3'), are consecutive-parallel.

The hydroperoxyl free radical $HO_2^{\bullet}$ formed in reaction (2) [11, 12] possesses an increased energy and, before its possible decomposition, can interact with a hydrogen or oxygen molecule, as the third body in reaction (3) or (4), respectively. The hydroxyl radical $HO^{\bullet}$ that appears in reaction (3) (the first variant) and disap-

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[1] Without allowance for possible intramolecular hydrogen bonding in the $HO_4^{\bullet}$ radical, for which $\Delta H^{\circ}_{f\,298}(HO_4^{\bullet}) = 122.6 \pm 13.7$ kJ mol^{-1} calculated from the data reported in [10].
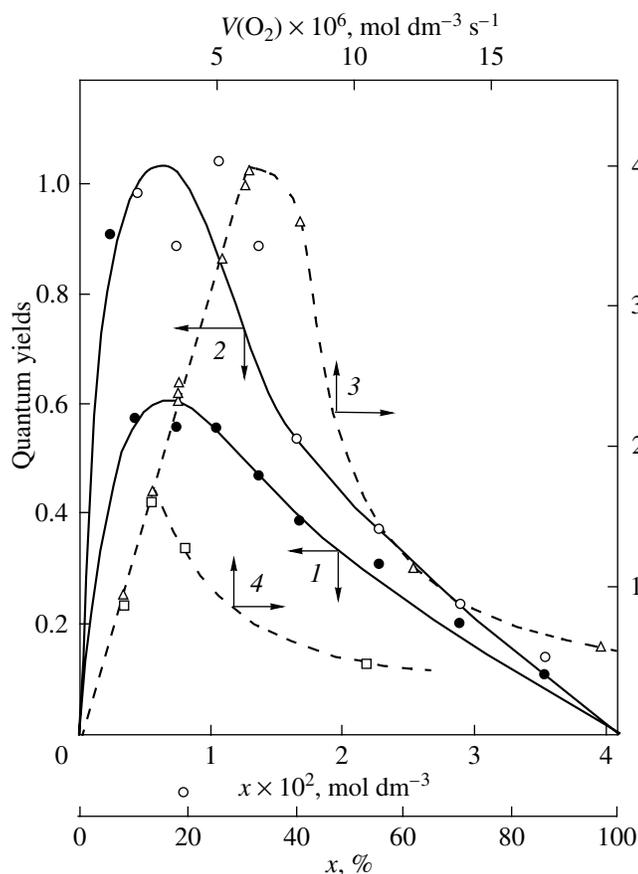
Fig. 1. (*1, 2*) Quantum yields of hydrogen peroxide and water, respectively, during the photochemical oxidation of hydrogen (λ_{irr} = 171.9–172.5 nm, a total pressure of 10^5 Pa, room temperature [5]) as a function of the initial oxygen concentration *x* in the hydrogen–oxygen system. (*3, 4*) Hydrogen peroxide formation rate $V(H_2O_2)$ (dashed curves) as a function of the flow rate of molecular oxygen ($V(O_2)$) through the discharge tube with atomic and molecular hydrogen, respectively, with the atomic hydrogen being preliminarily obtained in the discharge tube from molecular hydrogen (total pressure, 25–77 Pa; temperature, 77 K [6]). The symbols represent experimental data.

Fig. 2. (*1*) Reconstraction of the functional dependence of the total rate $V_{3.7}(H_2O_2)$ of hydrogen peroxide formation on the initial dissolved-oxygen concentration *x* from empirical data (symbols) for γ-radiolysis of water saturated with hydrogen and containing various amounts of oxygen [7] using Eqs. (Ia) and (IIIa) (model optimization in respect of the parameter α; the standard deviation of the function approximation is $S_Y = 1.13 \times 10^{-8}$). (*2*) The dashed curve describes the rate $V_3(H_2O_2)$ as a function of the initial oxygen concentration *x* based on Eq. (Ia) only and the same data (optimization by α; $S_Y = 1.73 \times 10^{-8}$).

pears in reaction (3') will possess additional energy due to the exothermicity of the first variant of reaction (3), whose heat is distributed between the two products. Hence, this radical should have a high enough reactivity to avoid accumulation in the system in the course of these reactions, whose rates should be equal $V_3 = V_{3'}$ under quasi-steady-state conditions. The hydrogen atom is regenerated in reactions (3) (the second variant given in parenthesis) and (3'). It was assumed [2, 8] that the hydrotetraoxyl radical $HO_4^{\bullet}$ (first suggested in [13]) produced in endothermic reaction (4), which was shown by mathematical analysis [1, 2, 8] to be responsible for the maximum on the experimental curve (Fig. 2), exists in the closed form of the five-membered
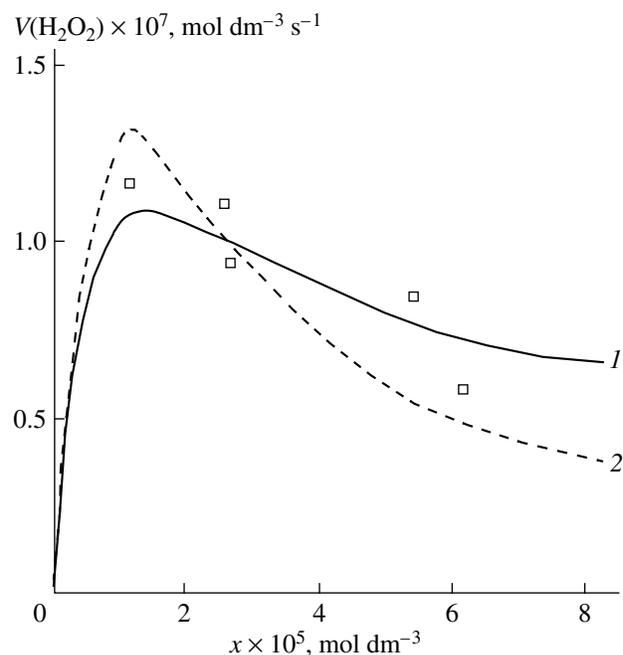
cycle $[\overline{OO-H\cdots OO}]^{\bullet}$ due to weak intramolecular hydrogen bonding [14, 15], a structure that imparts additional stability to this radical and makes it least reactive.

The radical $HO_4^{\bullet}$ was revealed by Staehelin et al. [16] in a pulse radiolysis study of ozone degradation in water; its UV spectrum with an absorption maximum at 260 nm ($\varepsilon(HO_4^{\bullet})_{280\ nm}$ = 320 ± 15 $m^2\ mol^{-1}$) was reported. The spectrum of the $HO_4^{\bullet}$ radical is similar to that of ozone, but its molar absorption coefficient $\varepsilon(HO_4^{\bullet})_{\lambda_{max}}$ is almost twofold higher [16]. The assumption about the cyclic structure of the $HO_4^{\bullet}$ radical[2] can stem from the fact that its mean lifetime (3.6 ± 0.4) ×

[2] The quantum-chemical calculation by the Gaussian-98 Program using the MP2/6-311++G** method made by I. V. Trushkov (Faculty of Chemistry, Moscow State University) confirmed a higher gain in energy (by 4.8 kJ mol^{-1}) of the cyclic structure for this radical relative to the helical structure calculated by the same method [17].
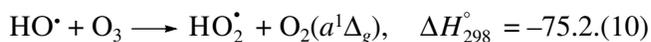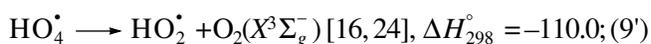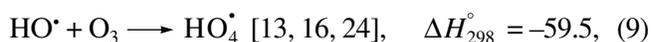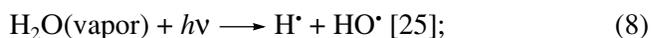
10^{-5} s in water at a temperature of 294 K (estimated in [3] from the value of $1/k$ for the reaction $HO_4^\bullet \xrightarrow{k} HO_2^\bullet + O_2$ [16]) is 3.9 times longer than that of the linear $HO_3^\bullet$ radical [17, 18] estimated in a similar manner in [3] for the same conditions [19]. Note that the hydrogen-bonded planar six-membered cyclic dimer $(HO_2^\bullet)_2$ was calculated in [20].

Low-reactive $HO_4^\bullet$ radicals along with $H^\bullet$ atoms take part in quadratic chain termination reactions of three types: $H^\bullet + H^\bullet$ [+M] (5), $H^\bullet + HO_4^\bullet$ (6), and $HO_4^\bullet + HO_4^\bullet$ (7). Reaction (4) and, to a much lesser degree, reaction (6) inhibit the chain process, because they results in inefficient consumption of its main participants, the $HO_2^\bullet$ and $H^\bullet$ species.

The hydrogen molecule that appears in reaction (5) possesses an excess energy if the reaction occurs in the gas phase and, to acquire stability on the assumption used in this work, should have time to deactivate via collision with a particle M that takes the excess energy [21]. To simplify the form of the kinetic equations, it was assumed that the rate of the bimolecular deactivation of the molecule substantially exceeds the rate of its unimolecular decomposition–the reverse step of reaction (5) of recombination of $H^\bullet$ atoms [9]. In reactions (6) and (7), hydrogen and oxygen are regenerated (in the form of $O_2(X^3\Sigma_g^-)$ molecules, including the singlet states $\Delta H_{f\,298}^\circ(O_2, a^1\Delta_g) = 94.3$ kJ mol^{-1} [10, 22] and $\Delta H_{f\,298}^\circ(O_2, b^1\Sigma_g^+) = 161.4$ kJ mol^{-1} [22], which are deactivated in collisions, and in part O_3) and the non-chain formation of hydrogen peroxide or water occurs, presumably, via the intermediate formation of the unstable hydrogen tetraoxide molecule H_2O_4 [20, 23]. Ozone does not interact with molecular hydrogen. At moderate temperatures, it decomposes at relatively low rate, especially, in the presence of $O_2(X^3\Sigma_g^-)$ [22]. The reaction of ozone with $H^\bullet$ atoms, which is not inconceivable, results in their replacement with $HO^\bullet$ free radicals.

The low-reactive hydrotetraoxyl $HO_4^\bullet$ radical [16] may be an intermediate in the process of the effective absorption and transformation of biologically hazardous UV radiation energy the Earth upper atmosphere. The potential energy surface for the atmospheric reaction $HO^\bullet + O_3$ was calculated by the DMBE method [24], in which the adduct $HO_4^\bullet(^2A)$ was considered as an intermediate. From this point of view, the following reactions (the corresponding values of ΔH_{298}° in the

standard state are given in kJ mol^{-1} [10]) are possible in the upper troposphere, as well as in the lower and middle stratosphere, where the main ozone layer is situated at an altitude of 16–30 km (temperature, 217–227 K; pressure, 1.0×10^4–1.2×10^3 Pa) [25]:

$$H_2O(\text{vapor}) + h\nu \longrightarrow H^\bullet + HO^\bullet \text{ [25]}; \tag{8}$$

$$HO^\bullet + O_3 \longrightarrow HO_4^\bullet \text{ [13, 16, 24]}, \quad \Delta H_{298}^\circ = -59.5, \tag{9}$$

$$HO_4^\bullet \longrightarrow HO_2^\bullet + O_2(X^3\Sigma_g^-) \text{ [16, 24]}, \Delta H_{298}^\circ = -110.0; \tag{9'}$$

$$HO^\bullet + O_3 \longrightarrow HO_2^\bullet + O_2(a^1\Delta_g), \quad \Delta H_{298}^\circ = -75.2. \tag{10}$$

The $HO_4^\bullet$, radical can decay via disproportionation with a molecule, radical, or atom in addition to dissociation. Note that $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ emission is observed at an altitudes of 30–80 and 40–130 km, respectively [26].

Staehelin et al. [16] pointed out that, in natural systems in which concentrations of intermediates are often very low, kinetic chains in chain reactions can be very long in the absence of scavengers, since the rates of chain termination reactions decreases with a decrease in the concentrations of transients according to the quadratic law, whereas the rates of chain propagation reactions varies according to the linear law.

The kinetic description of the noncatalytic oxidation of hydrogen, in particular, in an inert medium [21], according to the simplified scheme of free-radical non-branched-chain reactions (2)–(7) with a substantial excess of hydrogen over oxygen concentration was obtained by means of quasi-steady-state treatment, as it had been done in the previous studies on the kinetics of the branched-chain free-radical oxidation of hydrogen [11], despite the insufficient validity of this method in the latter case as applied to the non-steady-state occurrence of the process. The method was used with the following condition[3] for the first stages of the process: $k_6 = \sqrt{2k_5 2k_7}$ and $V_1 = V_5 + 2V_6 + V_7 = (\sqrt{2k_5}\,[H^\bullet] + \sqrt{2k_7}\,[HO_4^\bullet])^2$, which allow the power index of the term $d[H^\bullet]/dt$ in the equation $2k_5[H^\bullet]^2 = 0$ to be reduced to 1 [1]. The kinetic equations were derived for the rates (mol dm^{-3} s^{-1}) of the elementary reactions for the formation of molecular products of hydrogen oxidation.

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[3] For example, the ratio of the rate constants of the bimolecular disproportionation or dimerization of free radicals at room temperature is $k(HO^\bullet + HO_2^\bullet)/[2k(2HO^\bullet)2k(2HO_2^\bullet)]^{0.5} = 2.8$ in the atmosphere [25] and $k(H^\bullet + HO^\bullet)/[2k(2H^\bullet)2k(2HO^\bullet)]^{0.5} = 1.5$ in water [27], values that are close enough to unity.

The rate of the chain formation of hydrogen peroxide in propagation reaction (3) and of water in reactions (3) and (3') with $V_{3,3'}(H_2O) = 2V_3$ is

$$V_3(H_2O_2; H_2O) = V_{3'}(H_2O) = V_1\alpha lk_2x/f = \quad \text{(I)}$$

$$= V_1\alpha lx/f_m. \quad \text{(Ia)}$$

In this equation, V_1 is the initiation rate, $l = [H_2]$ and $x = [O_2]$ are the initial molar concentrations of the reactants with $l \gg x$; $\alpha = k_3/k_4$ is the ratio of the rate constants of the competing (parallel) reactions; $k_2 = \alpha l_m\sqrt{2k_5V_1}/x_m^2$ is the rate constant of reaction (2) of hydrogen atom addition to the oxygen molecule, whose analytical expression is defined by the solution to the quadratic equation derived from the condition of the extremum of the rate function $\partial V_3/\partial x = 0$; l_m and x_m are the concentrations of the components l and x, respectively, at the maximum of the function; $f = k_2x^2 + (\alpha l + x)\sqrt{2k_5V_1}$ and $f_m = x^2 + (\alpha l + x)x_m^2/\alpha l_m$; and $2k_5$ is the rate constant of hydrogen atom recombination reaction (5) considered to be bimolecular in this approximation.

The rate constant $2k_5$ for the case of pulse radiolysis of ammonia–oxygen gaseous mixtures at a total (with argon) pressure of 10^5 Pa and a temperature of 349 K was calculated as 1.6×10^8 dm^3 mol^{-1} s^{-1} [7] (a similar value for this rate constant in the gas phase was given in [28]). Pagsberg et al. [7] also found that the dependence of the yield of the intermediate HO$^{\bullet}$ on the oxygen concentration has a maximum close to 5×10^{-4} mol dm^{-3}. In the computer simulation of the process, they considered the strongly exothermic reaction $HO_2^{\bullet} + NH_3 \longrightarrow H_2O + {}^{\bullet}NHOH$, which is similar to reaction (3) given above, whereas the competing reaction (4) was not taken into account.

The ratio of the rates of the competing reactions is $V_3/V_4 = \alpha l/x$ and the chain length is $\nu = V_3/V_1$. Equation (Ia) was obtained by substitution of the rate constant k_2 into Eq. (I) with its analytical expression (in order to reduce the number of unknown parameters that are to be measured directly).

The rates of nonchain formation of hydrogen peroxide and water in reactions (6) and (7) of quadratic chain termination are as follows:

$$2V_6 = 2V_1\sqrt{2k_5V_1}(\alpha l + x)k_2x^2/f^2, \quad \text{(II)}$$

$$V_7 = V_1(k_2x^2)^2/f^2. \quad \text{(III)}$$

The designations of the parameters in this equation are the same as in Eq. (I).

The rate of the nonbranched-chain free-radical oxidation of hydrogen is a complex function of the rates of formation and decay of H$^{\bullet}$ atoms and HO$_4^{\bullet}$: radicals: $V_1 + V_{3,3'} - V_4 - V_5 + V_7$. Unlike the dependences of the

rates V_4 ($V_4 \le V_1$), V_5 and V_7, the dependences of the rates V_2, $V_{3;3'}$, and $2V_6$ on the oxygen concentration x show a maximum.

Equation (I) with the conditions (a) $k_2x^2 \ll (\alpha l + x)\sqrt{2k_5V_1}$, $\alpha l \gg x$ and (b) $k_2x^2 \gg (\alpha l + x)\sqrt{2k_5V_1}$, corresponding to the ascending and descending branches of the curve with a maximum can be transformed into simple directly and inversely proportional functions of concentration x, which allow preliminary estimation of the parameters k_2 and α:

$$V_3 = \sqrt{V_1}k_2x/\sqrt{2k_5}, \quad \text{(IV)}$$

$$V_3 = V_1\alpha l/\varphi x, \quad \text{(V)}$$

where $\varphi = 2$ at maximum when $k_2x^2 \cong (\alpha l + x)\sqrt{2k_5V_1}$, and $\varphi = 1$ at the decreasing part of the curve.

In the case of a lack of hydrogen excess in the hydrogen–oxygen system and possibility of direct capture by the homomolecular dimer $(O_2)_2$ [29, 30], which exists at low concentrations (depending on pressure and temperature) in equilibrium with O_2 [22], of the H$^{\bullet}$ atom yielding the heteronuclear cluster[4] HO$_4^{\bullet}$ (H$^{\bullet}$ + $(O_2)_2 \xrightarrow{k_{add}}$ HO$_4^{\bullet}$) more stable than $(O_2)_2$ [22], which cannot abstract a hydrogen atom from the hydrogen molecule, the nonchain hydrogen oxidation will occur ($k_2 = k_3 = k_4 = 0$) to give molecular oxidation products in the disproportionation of free radicals via reactions (6) and (7). The rates of these reactions are defined by modified Eqs. (II) and (III), in which $(\alpha l + x)$ is replaced with 1 and k_2 with $k_{add}K_{eq}$, the effective rate constant of H$^{\bullet}$ atom addition to the $(O_2)_2$ dimer ($K_{eq} = k/k'$ is the equilibrium constant of the reversible reaction $2O_2 \underset{k'}{\overset{k}{\rightleftarrows}} (O_2)_2$, and $k' \gg k_{add}$ [H$^{\bullet}$]). The formation rates of the stable products of nonchain oxidation ($k_3 = 0$), providing that either both reactions (2) and (4) or reaction (2) alone occur ($k_4 = 0$), are expressed by transformed Eqs. (II) and (III), in which $(\alpha l + x)$ is replaced with 1 and x^2 is replaced with x. In the latter case, the HO$_2^{\bullet}$ radical, rather than HO$_4^{\bullet}$, takes part in reactions (6) and (7).

Curve 1 in Fig. 2 describes in terms of the overall equation $V_{3,7} = V_1x(\alpha lf_m + x^3)/f_m^2$ for the rates of reactions (3) and (7) (which was derived on the basis of Eqs (Ia) and (III), respectively, where the latter is in the form $V_7 = V_1x^4/f_m^2$ (IIIa) in which k_2 is replaced with its analytical expression) the dependence of the rate of

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[4] Note that it is impossible to discriminate between the two-step bimolecular interaction of three bodies proceeding via the equilibrium formation of the labile intermediate compound $(O_2)_2$ and the elementary termolecular reaction $O_2 + O_2 + H^{\bullet} \longrightarrow HO_4^{\bullet}$.

hydrogen peroxide formation (minus the rate $V_{H_2O_2} = 5.19 \times 10^{-8}$ mol dm^{-3} s^{-1} of the primary formation of hydrogen peroxide after completion of the reactions in spurs) on the initial concentration of dissolved oxygen during the γ-radiolysis of water saturated with hydrogen (7×10^{-4} mol dm^{-3}) at a temperature of 296 K [4]. These data were calculated in the present work from the slopes of the initial parts of the curves of hydrogen peroxide buildup with dose at a ^{60}Co γ-radiation dose rate of $P = 0.67$ Gy s^{-1} and absorbed doses of $D \cong 22.5$–304.0 Gy. The following values of the primary radiation-chemical yields (in particles per 100 eV of energy absorbed) of water γ-radiolysis products in the bulk of solution at pH 4–9 and room temperature were used (taking into account that $V = GP$ and $V_1 = G_H P$): $G_{H_2O_2} = 0.75$ and $G_H = 0.6$ (initiation yield) [27]; $V_1 = 4.15 \times 10^{-8}$ mol dm^{-3} s^{-1}; and $2k_5 = 2.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1} [27].

As is seen from Fig. 2, the best description of the data with an increase in the oxygen concentration in water is attained when the rate V_3 of the chain formation of hydrogen peroxide via the propagation reaction (3) (curve 2, the obtained value of α is 0.11 ± 0.026) is taken into account in addition to the rate V_7 of the formation of this product via the nonchain mechanism in chain termination reaction (7) (curve 1, $\alpha = (8.5 \pm 2) \times 10^{-2}$). The value for the rate constant of addition reaction (2) determined from α is substantially underestimated $k_2 = 1.34 \times 10^7$ (vs. 2.0×10^{10} [27]) dm^3 mol^{-1} s^{-1}, a difference that can be accounted for by the radiation-chemistry specifics of the process that was not considered in the kinetic description of the experimental data, in particular, the oxygen consumption in reactions that are not involved in the employed hydrogen oxidation scheme [3] or reverse reactions resulting in the degradation of hydrogen peroxide by transient products of water radiolysis (e_{aq}^-, H$^•$, and HO$^•$), with the major role being played by the hydrated electron [27].

Thus, the addition reaction of the HO$_2^•$, radical that possesses an elevated energy in statu nascendi with the oxygen molecule (at sufficiently high oxygen concentrations) to give the HO$_4^•$ radical was used for the first time in the kinetic description of the initiated hydrogen oxidation at moderate temperature and pressure [2, 8]. This reaction is endothermic and competes with the chain propagation reaction via the H$^•$ atom. The HO$_4^•$ radical generated in the former reaction has a low reactivity and inhibits the chain reaction. In this context, it should be pointed out that the phenomenon of the progressive inhibition of nonbranched-chain free-radical processes with an increase (after attaining the highest reaction rate) in the concentration of an unsaturated compound (as a source of low-reactive free-radicals) can be elements of the self-regulation system of natural processes that returns them to a stable stationary state.

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