Free-Radical Nonbranched-Chain Oxidation of Hydrogen

Michael M. Silaev

Abstract—New reaction scheme is suggested for the initiated nonbranched-chain addition of hydrogen atoms to the multiple bond of the molecular oxygen. The scheme includes the addition reaction of the hydroperoxyl free radical to the oxygen molecule to form the hydrotetraoxyl free radical which is relatively low-reactive and inhibits the chain process by shortening of the kinetic chain length. This reaction competes with chain propagation reactions through a hydrogen atom. Based on the proposed scheme rate equations (containing one to three parameters to be determined directly) are deduced using quasi-steady-state treatment. The kinetic description with use the obtained rate equations is applied to the γ-induced nonbranched-chain process of the free-radical oxidation of hydrogen dissolved in water containing different amounts of oxygen at 296 K. The ratio of rate constants of competing reactions and the rate constant of the addition reaction to the molecular oxygen are defined. In this process the oxygen with the increase of its concentration begins to act as an oxidation autoinhibitor (or an antioxidant), and the rate of hydrogen peroxide formation as a function of the dissolved oxygen concentration has a maximum. From the energetic standpoint possible nonchain pathways of the free-radical oxidation of hydrogen and the routes of ozone decay *via* the reaction with the hydroxyl free radical (including the addition yielding the hydrotetraoxyl free radical) in the Earth's upper atmosphere were considered.

Index Terms—competition, hydrogen, low-reactive hydrotetraoxyl free radical, thermochemical data, energy.

I.   INTRODUCTION

The kinetics of inhibition for nonbranched-chain processes of saturated free-radical addition 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]. In these processes a low-reactive free radical is formed in the reaction competing with chain propagation reactions through a reactive free radical. In the present work the kinetics of inhibition by low-reactive hydrotetraoxyl free radical is considered for the nonbranched-chain process of the addition of a hydrogen atom to one of the two multiply bonded atoms of the oxygen molecule yielding a hydroperoxyl free radical. The hydroperoxyl free radical then abstracts the most labile atom from a molecule of the compound being oxidized or decomposes to turn into a molecule of an oxidation product. The only reaction that can compete with these two reactions at the chain evolution stage is the addition of the peroxyl radical to the oxygen molecule (provided that the oxygen concentration is sufficiently high). This reaction yields the secondary hydrotetraoxyl 1:2 adduct radical, which is the heaviest and the largest among the reactants. It is less reactive than the primary peroxyl 1:1 adduct radical and, as a consequence, does not participate in further chain propagation. At moderate temperatures, the reaction proceeds *via* a nonbranched-chain mechanism.

The aim of this study was the mathematical simulation of oxidation process autoinhibited by oxygen, when the dependence of the peroxide formation rate on the dissolved oxygen concentration has a maximum. The simulation was based on experimental data obtained for γ-radiation-induced addition reaction of hydrogen atom to the molecular oxygen for which the initiation rate V_1 is known (taking into account that $V = GP$ and $V_1 = G(\mathrm{H}^{\bullet})P$, where P is the dose rate, and $G(\mathrm{H}^{\bullet})$ is the initial yield of the chain-carrier hydrogen atom $\mathrm{H}^{\bullet}$ – initiation yield [2, 3]).

Based on the reaction scheme suggested for the kinetic description of the addition process to oxygen, the kinetic equations with one to three parameters to be determined directly were derived. Reducing the number of unknown parameters in a kinetic equation will allow one to decrease the narrowness of the correlation of these parameters and to avoid a sharp buildup of the statistical error in the nonlinear estimation of these parameters in the case of a limited number of experimental data points. The rate constant of the addition to oxygen, estimated as a kinetic parameter, can be compared to its reference value if the latter is known. This provides a clear criterion to validate the mathematical description against experimental data.

II.   KINETICS OF HYDROGEN ATOM ADDITION TO THE OXYGEN MOLECULE

A number of experimental findings concerning the autoinhibiting effect of an increasing oxygen concentration at modest temperatures on hydrogen

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oxidation both in the gas phase [4–6] (Fig. 2) and in the liquid phase [7] (Fig. 1, curve *2*), considered in my earlier works [8–11], can also be explained in terms of the competition kinetics of free radical addition [12, 13]. From Fig. 2 shows that the quantum yields of hydrogen peroxide and water (of products of photochemical oxidation of hydrogen at atmospheric pressure and room temperature) are maximum in the region of small concentrations of oxygen in the hydrogen–oxygen system (curves *1* and *2*, respectively) [4].

In the familiar monograph "Chain Reactions" by Semenov [14], it is noted that raising the oxygen concentration when it is already sufficient usually slows down the oxidation process by shortening the chains. The existence of the upper (second) ignition limit in oxidation is due to chain termination in the bulk through triple collisions between an active species of the chain reaction and two oxygen molecules (at sufficiently high oxygen partial pressures). In the gas phase at atmospheric pressure, the number of triple collisions is roughly estimated to be 10^3 times smaller than the number of binary collisions (and the probability of a reaction taking place depends on the specificity of the action of the third particle). Note that in the case of a gas-phase oxidation of hydrogen at low pressures of 25-77 Pa and a temperature of 77 K [5] when triple collisions are unlikely, the dependence of the rate of hydrogen peroxide formation on oxygen concentration (the rate of passing of molecular oxygen *via* the reaction tube) also has a pronounced maximum (see curves *3* and *4* in Fig. 2) that indicates a chemical mechanism providing the appearance of a maximum (see reaction 4 of *Scheme*).
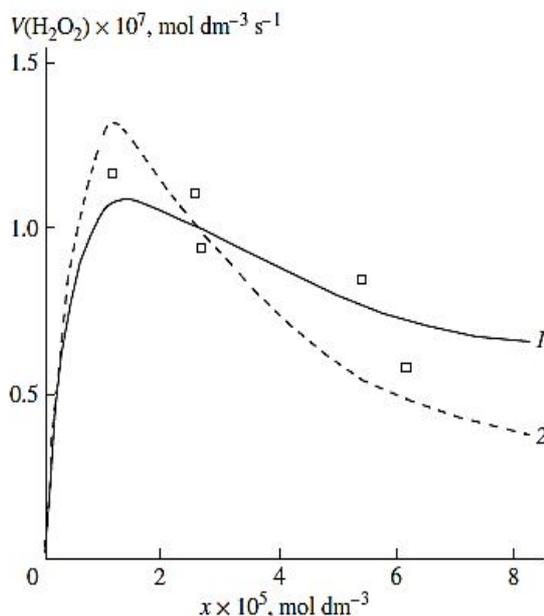
Figure 2. (*1, 2*) Quantum yields of (*1*, ●) hydrogen peroxide and (*2*, ○) water resulting from the photochemical oxidation of hydrogen in the hydrogen–oxygen system as a function of the oxygen concentration x (light wavelength of 171.9-172.5 nm, total pressure of 10^5 Pa, room temperature [4]). (*3, 4*) Hydrogen peroxide formation rate $V(H_2O_2)$ (dashed curves) as a function of the rate $V(O_2)$ at which molecular oxygen is passed through a gas-discharge tube filled with (*3*, △) atomic and (*4*, □) molecular hydrogen. Atomic hydrogen was obtained from molecular hydrogen in the gas-discharge tube before the measurements (total pressure of 25-77 Pa, temperature of 77 K [5]). The symbols represent experimental data.

Scheme

Nonbranched-chain oxidation of hydrogen and changes in enthalpy (ΔH_{298}°, kJ mol^{-1}) for elementary reactions[1]

Chain initiation

1. $H_2 \xrightarrow{hv, \gamma} 2H^{\bullet}$, $\Delta H_{298}^{\circ} = 436.0 \pm 0.0.$

Figure 1. (*1*, □) Reconstruction of the functional dependence of the total hydrogen peroxide formation rate $V_{3, 7}(H_2O_2)$ on the dissolved oxygen concentration x from empirical data (symbols) using Eqs. (1a) and (4a) (model optimization with respect to the parameter α) for the γ-radiolysis of water saturated with hydrogen and containing different amounts of oxygen at 296 K [7] ($S_Y = 1.13 \times 10^{-8}$). (2) The dashed curve described $V_3(H_2O_2)$ as a function of the oxygen concentration x based on Eq. (1a) (model optimization with respect to α) and the experimental data of curve 2 ($S_Y = 1.73 \times 10^{-8}$).
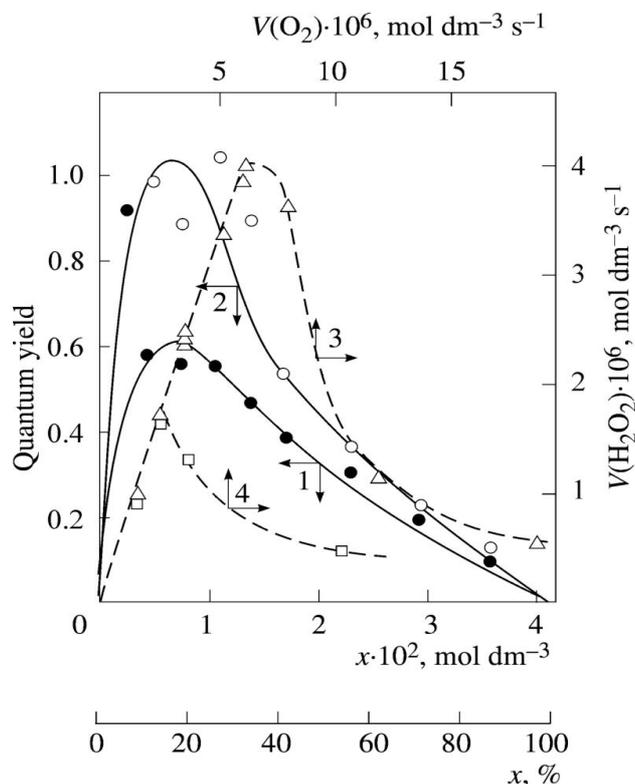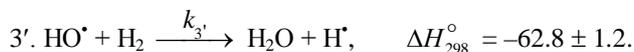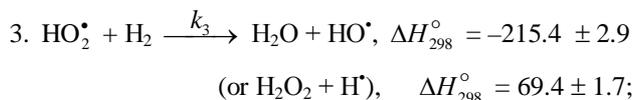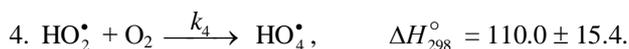
[1]According to Francisco and Williams [15], the enthalpy of formation ($\Delta H_f^{\circ}{}_{298}$) in the gas phase of $H^{\bullet}$, $HO^{\bullet}$, $HO_2^{\bullet}$, $HO_4^{\bullet}$ (the latter without the possible intramolecular hydrogen bond taken into account), O_3, H_2O [6], H_2O_2, and H_2O_4 is 218.0 ± 0.0, 39.0 ± 1.2, 12.6 ± 1.7, 122.6 ± 13.7, 143.1 ± 1.7, -241.8 ± 0.0, -136.0 ± 0, and -26.0 ± 9 kJ mol^{-1}, recspectively. Calculations for the $HO_4^{\bullet}$ radical with a helical structure were carried out using the G2(MP2) method [16]. The stabilization energies of $HO_2^{\bullet}$, $HO_4^{\bullet}$, and $HO_3^{\bullet}$ were calculated in the same work to be 64.5 ± 0.1, 69.5 ± 0.8, and 88.5 ± 0.8 kJ mol^{-1}, respectively. The types of the O_4 molecular dimers, their IR spectra, and higher oxygen oligomers were reported [17, 18]. The structure and IR spectrum of the hypothetical cyclotetraoxygen molecule O_4, a species with a high energy density, were calculated by the CCSD method, and its enthalpy of formation was estimated [19]. The photochemical properties of O_4 and the van der Waals nature of the O_2–O_2 bond were investigated [20, 21]. The most stable geometry of the dimer is two O_2 molecules parallel to one another. The O_4 molecule was identified by NR mass spectrometry [22].
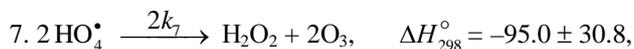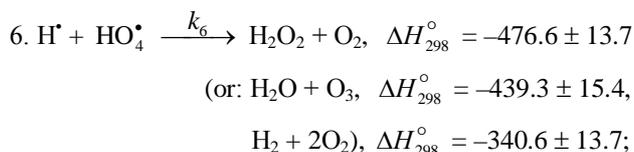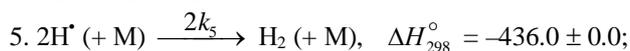
Chain propagation

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

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

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

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

Inhibition

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

Chain termination

5. $2H^{\bullet} (+ M) \xrightarrow{2k_5} H_2 (+ M)$, $\quad \Delta H^{\circ}_{298} = -436.0 \pm 0.0$;

6. $H^{\bullet} + HO_4^{\bullet} \xrightarrow{k_6} H_2O_2 + O_2$, $\Delta H^{\circ}_{298} = -476.6 \pm 13.7$

$\qquad$ (or: $H_2O + O_3$, $\Delta H^{\circ}_{298} = -439.3 \pm 15.4$,

$\qquad\qquad H_2 + 2O_2$), $\Delta H^{\circ}_{298} = -340.6 \pm 13.7$;

7. $2HO_4^{\bullet} \xrightarrow{2k_7} H_2O_2 + 2O_3$, $\quad \Delta H^{\circ}_{298} = -95.0 \pm 30.8$,

The chain evolution (propagation and inhibition) stage of the *Scheme* includes consecutive reaction pairs 2–3 and 3–3′; the parallel (competing) reaction pair 3–4; and consecutive–parallel reactions 2 and 4.

The hydroperoxyl free radical $HO_2^{\bullet}$ [23–26] resulting from reaction 2 possesses an increased energy due to the energy released the conversion of the O=O multiple bond into the HO–O$^{\bullet}$ ordinary bond. Therefore, before its possible decomposition, it can interact with a hydrogen or oxygen molecule as the third body *via* parallel (competing) reactions 3 and 4, respectively. The hydroxyl radical HO$^{\bullet}$ that appears and disappears in consecutive parallel reactions 3 (first variant) and 3′ possesses additional energy owing to the exothermicity of the first variant of reaction 3, whose heat is distributed between the two products. As a consequence, this radical has a sufficiently high reactivity not to accumulate in the system during these reactions, whose rates are equal ($V_3 = V_{3'}$) under quasi-steady-state conditions, according to the above scheme. Parallel reactions 3 (second, parenthesized variant) and 3′ regenerate hydrogen atoms. It is assumed [9, 10] that the hydrotetraoxyl radical $HO_4^{\bullet}$ (first reported in [27–29]) resulting from endothermic reaction 4, which is responsible for the peak in the experimental rate curve (Fig. 2, curve *3*), is closed into a five-membered $[\overline{OO-H\cdots OO}]^{\bullet}$ cycle due to weak intramolecular hydrogen bonding [30, 31]. This structure imparts additional stability to this radical and makes it least reactive.

The $HO_4^{\bullet}$ radical was discovered by Staehelin *et al.* [32] in a pulsed radiolysis study of ozone degradation in water; its UV spectrum with an absorption maximum at 260 nm ($\varepsilon(HO_4^{\bullet})_{280\,nm} = 320 \pm 15$ m^2 mol^{-1}) was reported.

The spectrum of the $HO_4^{\bullet}$ radical is similar to that of

ozone, but the molar absorption coefficient $\varepsilon(HO_4^{\bullet})_{\lambda_{max}}$ of the former is almost two times larger [32]. The assumption about the cyclic structure of the $HO_4^{\bullet}$ radical can stem from the fact that its mean lifetime in water at 294 K, which is $(3.6 \pm 0.4) \times 10^{-5}$ s (as estimated [11] from the value of $1/k$ for the monomolecular decay reaction $HO_4^{\bullet} \xrightarrow{k} HO_2^{\bullet} + O_2$ [32]), is 3.9 times longer than that of the linear $HO_3^{\bullet}$ radical [16, 33] estimated in the same way [11] for the same conditions [34], $(9.1 \pm 0.9) \times 10^{-6}$ s.

MP2/6-311++G** calculations using the Gaussian-98 program confirmed that the cyclic structure of $HO_4^{\bullet}$ [35] is energetically more favorable than the helical structure [16] (the difference in energy is 4.8–7.3 kJ mol^{-1}, depending on the computational method and the basis set).[2] For example, with the MP2(full)/6-31G(d) method, the difference between the full energies of the cyclic and acyclic $HO_4^{\bullet}$ conformers with their zero-point energies (ZPE) values taken into account (which reduces the energy difference by 1.1 kJ mol^{-1}) is –5.1 kJ mol^{-1} and the entropy of the acyclic-to-cyclic $HO_4^{\bullet}$ transition is

$\Delta S^{\circ}_{298} = -1.6$ kJ mol^{-1} K^{-1}. Therefore, under standard conditions, $HO_4^{\bullet}$ can exist in both forms, but the cyclic structure is obviously dominant (87%, $K_{eq} = 6.5$) [35].

Reaction 4 and, to a much lesser degree, reaction 6 inhibit the chain process, because they lead to inefficient consumption of its main participants – $HO_2^{\bullet}$ and H$^{\bullet}$.

The hydrogen molecule that results from reaction 5 in the gas bulk possesses an excess energy, and, to acquire stability within the approximation used in this work, it should have time for deactivation *via* collision with a particle M capable of accepting the excess energy [37]. 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 monomolecular decomposition, which is the reverse of reaction 5 [38].

Reactions[3] 6 and 7 regenerate hydrogen and oxygen (in the form of $O_2(X^3\Sigma^-_g)$) molecules, including the singlet states with $\Delta H^{\circ}_{f\,298}(O_2, a^1\Delta_g) = 94.3$ kJ mol^{-1} [15, 18]
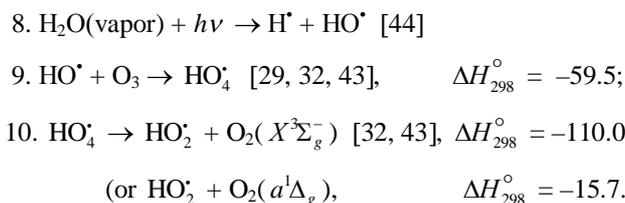
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[2]There were calculations for the two conformers (*cis* and *trans*) of the $HO_4^{\bullet}$ radical [36] using large scale *ab initio* methods and density functional techniques with extended basis sets. Both conformers have a nearly planar geometry with respect to the four oxygen atoms and present an unusually long central O–O bond. The most stable conformer of $HO_4^{\bullet}$ radical is the *cis* one, which is computed to be endothermic with respect to $HO_2^{\bullet}(X^2A'') + O_2(X^3\Sigma^-_g)$ at 0 K.

[3]Taking into account the principle of detailed balance for the various pathways of formation of products, whose numbers in the elementary reaction should not exceed three for possible involvement in the triple collisions in the case of the reverse reaction, since the probability of simultaneous interaction of four particles is negligible.

and $\Delta H^{\circ}_{f\,298}$ (O_2, $b^1\Sigma^+_g$) = 161.4 kJ mol^{-1} [18], which are deactivated by collisions, and in the form of O_3) and yield hydrogen peroxide or water *via* a nonchain mechanism, presumably through the intermediate formation of the unstable hydrogen tetraoxide molecule H_2O_4 [39, 40].[4] Ozone does not interact with molecular hydrogen. At moderate temperatures, it decomposes fairly slowly, particularly in the presence of O_2($X^3\Sigma^-_g$) [18]. The reaction of ozone with H$^{\bullet}$ atoms, which is not impossible, results in their replacement with HO$^{\bullet}$ radicals. The relative contributions from reactions 6 and 7 to the process kinetics can be roughly estimated from the corresponding enthalpy increments (*Scheme*).

When there is no excess hydrogen in the hydrogen–oxygen system and the homomolecular dimer O_4 [19–22, 41, 42], which exists at low concentrations (depending on the pressure and temperature) in equilibrium with O_2 [18], can directly capture the H$^{\bullet}$ atom to yield the heteronuclear cluster HO$^{\bullet}_4$,[5] which is more stable than O_4 [18] and cannot abstract a hydrogen atom from the hydrogen molecule, nonchain hydrogen oxidation will occur to give molecular oxidation products *via* the disproportionation of free radicals.

The low-reactive hydrotetraoxyl radical HO$^{\bullet}_4$ [32], which presumably has a high energy density [19], may be an intermediate in the efficient absorption and conversion of biologically hazardous UV radiation energy the Earth upper atmosphere. The potential energy surface for the atmospheric reaction HO$^{\bullet}$ + O_3, in which the adduct HO$^{\bullet}_4$(^2A) was considered as an intermediate, was calculated by the DMBE method [43]. From this standpoint, the following reactions are possible in the upper troposphere, as well as in the lower and middle stratosphere, where most of the ozone layer is situated (altitude of 16–30 km, temperature of 217–227 K, pressure of 1.0 × 10^4–1.2 × 10^3 Pa [44]; the corresponding ΔH°_{298} reaction values are given in kJ mol^{-1} [15]):

8. H_2O(vapor) + $h\nu \rightarrow$ H$^{\bullet}$ + HO$^{\bullet}$ [44]

9. HO$^{\bullet}$ + $O_3 \rightarrow$ HO$^{\bullet}_4$ [29, 32, 43], $\qquad \Delta H^{\circ}_{298}$ = –59.5;

10. HO$^{\bullet}_4 \rightarrow$ HO$^{\bullet}_2$ + O_2($X^3\Sigma^-_g$) [32, 43], ΔH°_{298} = –110.0

$\qquad$ (or HO$^{\bullet}_2$ + O_2($a^1\Delta_g$)), $\qquad\qquad \Delta H^{\circ}_{298}$ = –15.7.

The HO$^{\bullet}_4$ radical can disappear *via* disproportionation with a molecule, free radical, or atom in addition to

dissociation. Note that emission from O_2($a^1\Delta_g$) and O_2($b^1\Sigma^+_g$) is observed at altitudes of 30–80 and 40–130 km, respectively [45].

Staehelin *et al.* [32] pointed out that, in natural systems in which the 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 the chain termination reactions decrease with decreasing concentrations of the intermediates according to a quadratic law, whereas the rates of the chain propagation reactions decrease according to a linear law.

The kinetic description of the noncatalytic oxidation of hydrogen, including in an inert medium [37], in terms of the simplified scheme of free-radical nonbranched-chain reactions (*Scheme*), which considers only quadratic-law chain termination and ignores the surface effects [5], at moderate temperatures and pressures, in the absence of transitions to unsteady-state critical regimes, and at a substantial excess of the hydrogen concentration over the oxygen concentration was obtained by means of quasi-steady-state treatment, as in the previous studies on the kinetics of the branched-chain free-radical oxidation of hydrogen [46], even though the applicability of this method in the latter case under unsteady states conditions was insufficiently substantiated. The method was used with the following condition[6] for the first stages of the process: $k_6 = \sqrt{2k_5 2k_7}$ [47] and, hence, $V_1 = V_5 + 2V_6 + V_7 = (\sqrt{2k_5}$ [H$^{\bullet}$] $+\sqrt{2k_7}$ [HO$^{\bullet}_4$])^2 which allow the exponent of the $2k_5$[H$^{\bullet}$]^2 term in the d[H$^{\bullet}$]$/dt = 0$ equation to be reduced to 1 [1, 47]. 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.

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.

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

$$V_3(H_2O_2;\ H_2O) = V_{3'}(H_2O) = V_1\alpha l k_2 x/f \qquad (1)$$

$$= V_1\alpha l x/f_m \qquad (1a)$$

In this equation[7], V_1 is the initiation rate, l = [H_2] and x = [O_2] are the molar concentrations of the reactants with $l >> x$; $\alpha = k_3/k_4$ is the ratio of the rate constants of the competing (parallel) reactions; $k_2 = \alpha l_m\sqrt{2k_5 V_1}/x^2_m$ is the rate constant of reaction 2 of hydrogen atom addition to the oxygen molecule, whose analytical expression is

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[4]The planar, six-atom, cyclic, hydrogen-bonded dimer $(HO^{\bullet}_2)_2$ was calculated using quantum chemical methods (B3LYP density functional theory) [40]. The hydrogen bond energy is 47.7 and 49.4 kJ mol^{-1} at 298 K for the triplet and singlet states of the dimer, respectively.

[5]It is impossible to make a sharp distinction between the two-step bimolecular interaction of three species *via* the equilibrium formation of the labile intermediate O_4 and the elementary trimolecular reaction O_2 + O_2 + H$^{\bullet} \rightarrow$ HO$^{\bullet}_4$.

[6]For example, the ratio of the rate constants of the bimolecular disproportionation and dimerization of free radicals at room temperature is k(HO$^{\bullet}$ + HO$^{\bullet}_2$)/[$2k$(2HO$^{\bullet}$)$2k$(2HO$^{\bullet}_2$)]$^{0.5}$ = 2.8 in the atmosphere [44] and k(H$^{\bullet}$ + HO$^{\bullet}$)/[$2k$(2H$^{\bullet}$)$2k$(2HO$^{\bullet}$)]$^{0.5}$ = 1.5 in water [3]. These values that are fairly close to unity.

[7]This equation can be used to describe a wide range of nonbranched-chain reactions of addition of any free radicals to the C=C bonds of unsaturated hydrocarbons, alcohols, etc., which result in the formation of molecular 1:1 adducts in binary reaction systems of saturated and unsaturated components [1, 9, 10].

obtained 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 $2k_5$ in the case of the pulsed radiolysis of ammonia–oxygen (+ argon) gaseous mixtures at a total pressure of 10^5 Pa and a temperature of 349 K was calculated to be 1.6×10^8 dm^3 mol^{-1} s^{-1} [6] (a similar value of this constant for the gas phase was reported in an earlier publication [48]). Pagsberg *et al.* [6] 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$_3$ → H$_2$O + $^{\bullet}$NHOH, which is similar to reaction 3 in *Scheme*, 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 $v = V_3/V_1$. Equation (1a) was obtained by substitution of the rate constant k_2 into Eq. (1) with its analytical expression (in order to reduce the number of unknown parameters that are to be measured directly).The optimum concentration x_m of oxygen, at which the rate of oxidaton is maximum, can be calculated from Eq. (1a) or the analitical expression for k_2 if other parameters that appear in these expressions are known.

The rates of nonchain formation of molecular hydrogen, hydrogen peroxide, and water in reactions 5, 6, and 7 of quadratic chain termination are as follows:

$$V_5 = V_1^2 2k_5 \left(\alpha l + x\right)^2 / f^2 , \qquad (2)$$

$$2V_6 = 2V_1 \sqrt{2k_5V_1} \left(\alpha l + \beta + x\right) k_2 x^2 / f^2 , \qquad (3)$$

$$V_7 = V_1 \left(k_2 x^2\right)^2 / f^2 . \qquad (4)$$

The designations of the parameters in this equation are the same as in Eq. (1).

The rate of the nonbranched-chain free-radical oxidation of hydrogen is a complex function of the rates of formation and disappearance 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 ($V_4 \leq V_1$), 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 (1) under 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 equations which allow preliminary to estimate the parameters α and k_2 and express directly and inversely proportional functions of concentration x:

$$V_3 = \sqrt{V_1}k_2x / \sqrt{2k_5} , \qquad (5)$$

$$V_3 = V_1\alpha l / \varphi x , \qquad (6)$$

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

In the case of nonchain hydrogen oxidation *via* the above addition reaction (H$^{\bullet}$ + O$_4$ $\xrightarrow{k_{add}}$ HO$_4^{\bullet}$), the formation rates of the molecular oxidation products in reactions 6 and 7 (*Scheme*, $k_2 = k_3 = k_4 = 0$) are defined by modified Eqs. (3) and (4) in which $\beta = 0$, $(\alpha l + x)$ is replaced with 1, and k_2 is replaced with $k_{add}K_{eq}$ ($k_{add}K_{eq}$ is the effective rate constant of H$^{\bullet}$ addition to the O$_4$ dimer, $K_{eq} = k/k'$ is the equilibrium constant of the reversible reaction $2O_2 \underset{k'}{\overset{k}{\Longleftrightarrow}} O_4$ with $k' \gg k_{add}$[H$^{\bullet}$]). The formation rates of the stable products of nonchain oxidation ($k_3 = 0$), provided that either reactions 2 and 4 or reaction 2 alone ($k_4 = 0$) occurs (*Scheme*; in the latter case, reactions 6 and 7 involve the HO$_2^{\bullet}$ radical rather than HO$_4^{\bullet}$), are given by modified Eqs. (3) and (4), in witch $(\alpha l + x)$ replaced with 1, and x^2 replaced with x. In the latter case, the HO$_2^{\bullet}$ radical, rather than HO$_4^{\bullet}$, takes part in reactions 6 and 7.

It is important to note that, if in the *Scheme* chain initiation *via* reaction 1 is due to the interaction between molecular hydrogen and molecular oxygen yielding the hydroxyl radical HO$^{\bullet}$ instead of H$^{\bullet}$ atoms and if this radical reacts with an oxygen molecule (reaction 4) to form the hydrotrioxyl radical HO$_3^{\bullet}$ (which was obtained in the gas phase by neutralization reionization (NR) mass spectrometry [33] and has a lifetime of $>10^{-6}$ s at 298 K) and chain termination takes place *via* reactions 5–7 involving the HO$^{\bullet}$ and HO$_3^{\bullet}$, radicals instead of H$^{\bullet}$ and HO$_4^{\bullet}$, respectively, the expressions for the water chain formation rates derived in the same way will appear as a rational function of the oxygen concentration x without a maximum: $V_{3'}(\text{H}_2\text{O}) = V_1k_3l / (k_4x + \sqrt{2k_5V_1})$.

Curve *2* in Fig. 1 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 from Eqs. (1a) and (4), respectively, at that Eq. (4) in the form [49] of $V_7 = V_1x^4/f_m^2$ (4a) in which k_2 is replaced with its analytical expression $\alpha l_m \sqrt{2k_5V_1}/x_m^2$ derived from Eq. (1)), the dependence of the hydrogen peroxide formation rate (minus the rate $V_{\text{H}_2\text{O}_2} = 5.19 \times 10^{-8}$ mol dm^{-3} s^{-1} of the primary formation of hydrogen peroxide after completion of the reactions in spurs) on the concentration of dissolved oxygen during the γ-radiolysis of water saturated with hydrogen (at the initial concentration 7×10^{-4} mol dm^{-3}) at 296 K [7]. These data were calculated in the present work from the initial slopes of hydrogen peroxide buildup versus dose curves for 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 yield G (species per 100 eV of energy absorbed) for 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) [3]; $V_1 = 4.15 \times 10^{-8}$ mol dm^{-3} s^{-1}; $2k_5 = 2.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1} [3]. As can be seen from Fig. 1, the best description of the data with an increase in the oxygen concentration in water is attained when the rate V_7 of the formation of hydrogen peroxide *via* the nonchain mechanism in the chain termination reaction 7 (curve *1*, $\alpha = (8.5 \pm 2) \times 10^{-2}$) is taken into account in addition to the rate V_3 of the chain formation of this product *via* the propagation reaction 3 (dashed curve *2*, $\alpha = 0.11 \pm 0.026$). 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} [3]) dm^3 mol^{-1} s^{-1}. The difference can be due to the fact that the radiation-chemical specifics of the process were not considered in the kinetic description of the experimental data. These include oxygen consumption *via* reactions that are not involved in the hydrogen oxidation *Scheme* and reverse reactions resulting in the decomposition of hydrogen peroxide by intermediate products of water radiolysis (e_{aq}^-, H$^\bullet$, HO$^\bullet$), with the major role played by the hydrated electron [3].

III.   CONCLUSIONS

Thus, the addition reaction of the HO$_2^\bullet$ radical that possesses an elevated energy in statu nascendi with the oxygen molecule (at sufficiently high oxygen concentrations) to give the HO$_4^\bullet$ radical was used for the first time in the kinetic description of the initiated hydrogen oxidation at moderate temperature and pressure [9, 10]. This reaction is endothermic and competes with the chain propagation reaction *via* the H$^\bullet$ atom. The HO$_4^\bullet$ radical generated in the former reaction has a low reactivity and inhibits the chain reaction.[8]

The above data concerning the competition kinetics of the nonbranched-chain addition of hydrogen atoms to the multiple bonds of the oxygen molecules make it possible to describe, using rate equations (1a) and (4a), obtained by quasi-steady-state treatment, the peaking experimental dependences of the formation rates of molecular 1:1 adduct H$_2$O$_2$ on the concentration of the oxygen over the entire range of its variation in binary system (Fig. 1). In such reaction systems consisting of saturated and unsaturated components [51, 52], the unsaturated compound (in this case the O$_2$) is both a reactant and an autoinhibitor, specifically, a source of low-reactive free

radicals (in this case the HO$_4^\bullet$ radicals) shortening kinetic chains.

The progressive inhibition of the nonbranched-chain processes, which takes place as the concentration of the unsaturated compound is raised (after the maximum process rate is reached), can be an element of the self-regulation of the natural processes that returns them to the stable steady state.

Using mechanism of the nonbranched-chain free-radical hydrogen oxidation considered here, it has been demonstrated that, in the Earth's upper atmosphere, the decomposition of O$_3$ in its reaction with the HO$^\bullet$ radical can occur *via* the addition of the latter to the ozone molecule, yielding the HO$_4^\bullet$ radical, which is capable of efficiently absorbing UV radiation [32].

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[8]Note that in the case of similar nonbranched-chain (i.e., "slow") oxidation of RH hydrocarbons, the corresponding reactive RO$_2^\bullet$ and low-reactive RO$_4^\bullet$ radicals participate in the process [50]. The only difference between the kinetic model of oxidation and the kinetic model of the chain addition of 1-hydroxyalkyl radicals to the free (unsolvated) form of formaldehyde in nonmethanolic alcohol–formaldehyde systems [1, 9, 10] is that in the former does not include the formation of the molecular 1:1 adduct *via* reaction 4.

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