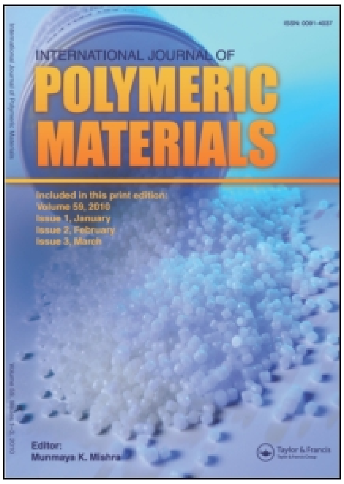

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Silaev, Michael M.(2000) 'The Competition Kinetics of Unbranched Chain Processes of Free-Radical Addition to Double Bonds of Molecules with the Formation of 1:1 Adducts', International Journal of Polymeric Materials, 46: 3, 435 — 449

To link to this Article: DOI: 10.1080/00914030008033886

URL: http://dx.doi.org/10.1080/00914030008033886

Intern. J. Polymeric Mater., 2000, Vol. 46, pp. 435–449
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The Competition Kinetics of Unbranched Chain Processes of Free-Radical Addition to Double Bonds of Molecules with the Formation of 1 : 1 Adducts

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(Received 10 November 1998)

Based on a kinetic model involving competing parallel reactions for free-radical addition to the double bond of a molecule with the formation of 1 : 1 adduct and participation of three radical types in the chain propagation, versions of the rate equation with 1–3 measurable parameters are derived. These versions make it possible to describe the non-monotonic (with maximum) dependence of the formation rate of an addition product on concentration of the unsaturated compound. The unbranched chain process occurs in binary liquid systems comprising saturated and unsaturated components at comparable concentrations. Application of the competition kinetics of free-radical addition to oxidation of some hydrocarbons is discussed when the reaction that competes with chain propagation reactions involving the alkylperoxy radical $RO_2^{\cdot}$ gives the cyclic alkylhydrotetraoxy radical $[\overline{R_{(-H)}O_4H}]$ as a less reactive radical inhibiting the chain process of formation of the main products of oxidation.

Keywords: Free-radical addition; double bonds; kinetics; 1 : 1 adducts

INTRODUCTION

Studies concerned with the kinetics of chain addition processes of free radicals from saturated compounds across the double bond of unsaturated compounds yielding only small molecules (without telomerization) and involving two types of active centers in chain propagation step (the two-center reaction scheme) – the chain propagation radical and the addition radical (adduct) – do not usually consider the competing (to chain propagation) reaction of abstraction of a weakly bound atom (for example, hydrogen) from the unsaturated molecule by the produced adduct radical [1]. Based on the schemes of these homogeneous processes in liquid phase, which do not involve the mentioned competing reaction, rate equations that define rate V as a monotonic function of concentration x of unsaturated compound are derived in terms the quasi-steady-state approximation. For example, an irrational function of the general form $V_1 = a_1x/(b_1x^2 + c_1x + d_1)^{1/2}$, given by Walling [1], where $a-d$ are the coefficients, is a particular case of the function for the rate of binary copolymerization (and it has been derived in a similar manner) with comparable concentrations of monomers, x_1 and x_2: $V_{12} = (a_{11}x_1^2 + a_{12}x_1x_2 + a_{22}x_2^2)/(b_{11}x_1^2 + c_{12}x_1 x_2 + d_{22}x_2^2)^{1/2}$, obtained on the assumption of rather long chains when it is possible, at the chain propagation step, to equalize the rates of two elementary consecutive reactions that both involve the same two radicals of different types. Allowance for a reaction that competes with the chain propagation reaction and yields the third type of radical (the three-center scheme) inhibiting the chain process was made in the previous work [2]. In that work, a rate equation of the form $V_m = (a_{02}x^2 + a_{01}x)/(bx^2 + cx + d)$ describing a nonmonotonic (with maximum) dependence of reaction rate on concentration of the unsaturated compound for unbranched chain processes of free-radical addition to the double bond of a molecule in binary systems that contain unsaturated and saturated components, the latter being in excess, was derived in terms of the quasi-steady-state approximation. In this work we derived a similar rate equation for the general case when the concentrations of the two components are comparable: $V = ax/(bx^2 + cx + d)$, and the competition kinetics of free-radical addition is applied to the case of oxidation of some hydrocarbons in liquid phase when the reaction that competes with chain propagation reactions involving the alkylperoxy radical $RO_2^{\cdot}$ gives the cyclic alkylhydrotetraoxy radical $[\overline{R_{(-H)}O_4H}]^{\cdot}$ as a less reactive radical inhibiting the chain process of formation of the main products of oxidation.

A KINETIC MODEL FOR ADDITION TO THE DOUBLE BOND OF AN ORGANIC COMPOUND

The most representative scheme for a widely occurring [2–9] liquid-phase competitive unbranched chain process of addition of a free radical from a saturated compound to the double bond of an unsaturated substance resulting in formation of small entities (primarily 1 : 1 adducts) includes the consecutive-parallel reactions **1**, **1a** and **2–7** [2, 3] (Scheme **I**). Under these conditions, the dependence of formation rate of the 1 : 1 adducts on concentration of an unsaturated compound usually passes through a maximum at a low concentration of the compound [2–7]. For a binary system which does not contain the saturated component in a large excess, it is necessary that the interaction of the initiating agent (radical $R_0^{\cdot}$) with both components be taken into account, thus suggesting an additional reaction **1b**. This kinetic model of free-radical addition to the double bond of an organic compound with participation of three radical types in the chain propagation is given by the following reaction scheme.

I. Chain initiation

1. $I \xrightarrow{2k_1} R_0^{\cdot} + R_0^{\cdot}$
1a. $R_0^{\cdot} + R_1A \xrightarrow{k_{1a}} R_0A + R_1^{\cdot}$
1b. $R_0^{\cdot} + R_2B \xrightarrow{k_{1b}} R_0B + R_2^{\cdot}$

II. Chain propagation

2. $R_1^{\cdot} + R_2B \xrightarrow{k_2} R_3^{\cdot}$
3. $R_3^{\cdot} + R_1A \xrightarrow{k_3} R_3A + R_1^{\cdot}$
4. $R_3^{\cdot} + R_2B \xrightarrow{k_4} R_3B + R_2^{\cdot}$

III. Chain termination

5. $R_1^{\cdot} + R_1^{\cdot} \xrightarrow{2k_5} \mathrm{Prod}_{(5)}$
6. $R_1^{\cdot} + R_2^{\cdot} \xrightarrow{k_6} \mathrm{Prod}_{(6)}$
7. $R_2^{\cdot} + R_2^{\cdot} \xrightarrow{2k_7} \mathrm{Prod}_{(7)}$

SCHEME I

Here **I** is the initiator, *e.g.*, peroxide [1, 8, 9]; $R_0^{\cdot}$ is some reactive radical; A and B are hydrogen [1–3, 8, 9] or halogen [4–7] atoms; $R_1^{\cdot}$

is PCl_2 [4,5] or CCl_3 [6], alkyl [1,7], α-hydroxyalkyl [1–3,8,9], or other functionally substituted radical [1] (the addend radical); $R_2^{\cdot}$ is the formyl [2,3,9], alkenyl (beginning with propenyl) [1,4–8], α-hydroxyalkenyl [2,3,8], or other functionally substituted radical [1]; $R_3^{\cdot}$ is the saturated adduct radical [1–9]; R_0A, R_0B, and R_1A are saturated compounds; R_2B is an unsaturated compound; R_3A and R_3B are the final (nonradical) products, the 1 : 1 adducts; and Prod are the final products of combination or disproportionation of radicals. Scheme **I** includes two pairs of competing reactions **1a** *vs.* **1b** and **3** *vs.* **4**.

Reaction **1** of chain initiation proceeds at a rate V_1 due to decomposition of chemical initiating agents [1,8,9] or exposure to light [1,8] or ionizing radiation [2–7]. The unsaturated radicals $R_2^{\cdot}$ produced in reactions **1b** and **4** are low-reactive (because of resonance stabilization [10]) and inhibit the addition process by cross combination reaction **6** with the chain-carrier radicals $R_1^{\cdot}$. The reaction of $R_2^{\cdot}$ radicals with the saturated component R_1A is energetically unfavorable, as it gives (by radical substitution at the hydrogen atom) the radical $R_1^{\cdot}$ that is less stable than $R_2^{\cdot}$ capable of resonance stabilization [10]. Plausible reaction

$$2a \cdot R_1^{\cdot} + R_2B \xrightarrow{k_{2a}} R_1B + R_2^{\cdot}$$

that is parallel to reaction **2** does not play any determining role in chain propagation and is unnecessary for kinetic description of the process since the rate ratio $V_2/V_{2a} = k_2/k_{2a}$ for these reactions is independent of concentration of the unsaturated component R_2B in the system. Other radical-molecule reactions are unlikely as shown previously [2]. The adduct radical $R_3^{\cdot}$ formed in reaction **2** has the highest mass and can possess a higher energy by virtue of difference in energies released upon double-to-single bond transformation, thus being capable of abstracting an H atom from neighboring component molecules within the matrix "cage" without escaping it. The 1 : 1 adducts are formed in reaction **3** of chain propagation (R_3A, the principal product of the chain process) and in competing reaction **4** that prevents the propagation (R_3B, the side product). The rate of the process of formation of 1 : 1 adducts is a complex function of formation and disappearance rates of radicals $R_1^{\cdot}$ and $R_2^{\cdot}$: $V(R_3A, R_3B) = V_2 = V_3 + V_4 = (V_{1a} + V_3 - V_5) - (V_{1b} + V_4 - V_7)$.

Equations to describe formation rates V_3 and V_4 (mol L^{-1} s^{-1}) of the R_3A and R_3B 1 : 1 adducts in the binary system with comparable concentrations of the components were derived in terms of Scheme **I**[1] are as follows:

$$V_3(R_3A) = \frac{[\gamma l/(\gamma l + x)]V_1 k_2 \alpha l x}{k_2 x^2 + (\alpha l + x)\sqrt{2k_5 V_1}}, \tag{1}$$

$$V_4(R_3B) = \frac{[\gamma l/(\gamma l + x)]V_1 k_2 x^2}{k_2 x^2 + (\alpha l + x)\sqrt{2k_5 V_1}}, \tag{2}$$

where $l = [R_1A] > [R_2B] = x$ is the initial molar concentration for reactants, k_2 is the rate constant for addition of a radical from the saturated component to the unsaturated reactant, $\alpha = k_3/k_4$ and $\gamma = k_{1a}/k_{1b}$ are the rate constant ratios of the relevant competing reactions. The rates of the competing reactions are in the ratio of $V_3/V_4 = \alpha l/x$ and the chain length is $v = V_3/V_1$.

A mathematical analysis [2] shows that involvement of radicals R_2 instead of adduct radicals R_3 in reactions with one another and with radicals R_1 at the chain propagation step ensures that the dependence of 1 : 1 adduct formation upon concentration of unsaturated compound passes through a maximum. In this case, reaction **1b** competing with reaction **1a** is responsible for the maximum on the rate dependence given by Eq. (2), whereas reaction **4** that competes with reaction **3** determines the maximum displayed by relationship (1).

To reduce the two concentration variables to a single variable in the rate equation for a binary system, the concentration may be expressed in terms of the corresponding mole fractions. Then the equation for the overall formation rate $V_2 = V_3 + V_4$ of the R_3A and R_3B 1 : 1 adducts (which can be identical, as in the case of R_3H [1–3, 8, 9]) in the system takes the forms

$$V_2(R_3A + R_3B) = \frac{[\gamma l/(\gamma l + x)]V_1 k_2 x(\alpha l + x)}{k_2 x^2 + (\alpha l + x)\sqrt{2k_5 V_1}} \tag{3}$$

$$= \frac{\{\gamma(1-\chi)/[\gamma(1-\chi)+\chi]\}V_1 k_2 \chi[\alpha(1-\chi)+\chi]}{k_2 \chi^2 + [\alpha(1-\chi)+\chi]\sqrt{2k_5 V_1}/(l+x)}, \tag{3a}$$

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[1] The equations were derived in the steady-state approximation using the condition $k_6 = \sqrt{2k_5 2k_7}$ and $V_1 = V_5 + 2V_6 + V_7 = (\sqrt{2k_5}[R_1] + \sqrt{2k_7}[R_2])^2$ that allowed the power index of term $2k_5[R_1]^2$ in equation $d[R_1]/dt = 0$ to be reduced from 2 to 1 [2].

where $1-\chi = l/(l+x)$ and $\chi = x/(l+x)$ are the mole fractions of the saturated and the unsaturated component, respectively ($0 < \chi < 1$). The condition of extremum of rate function (3) at $k_{1b} = 0$ ($[R_1A] \gg [R_2B]$), when $\gamma l/(\gamma l + x) = 1$, gives $k_2 = [(\sqrt{\alpha l_m}/x_m) + 1/\sqrt{\alpha l_m}]^2\sqrt{2k_5V_1}$, where x_m and l_m are the values of x and l at the maximum, respectively [3].

Physically, term $\gamma l/(\gamma l + x)$ in the numerator of rate Eqs. (1)–(3) is an analogue of the mole fraction of the saturated component. Therefore, when the excess of saturated component is low, it may be sufficient to introduce the mole fraction (or its analogue) of saturated component into the equation for initiation rate V_1 [2,3] instead of using the additional unknown γ in the expression for the rate of the process (*i.e.*, assuming $k_{1b} = 0$). In order to reduce the number of unknown parameters (k_2, α and γ), we can replace parameter γ by α (*i.e.*, assuming that $\gamma \cong \alpha$) in the rate equation since the chemical patterns of competing reactions **1a** and **1b** or **3** and **4** are identical. For example, the rate constant ratios for reactions of various radicals ($^{\cdot}OH$, $CH_3O^{\cdot}$, $^{\cdot}CH_3$, $NO_3^{\cdot}$, or $H_2PO_4^{\cdot}$) with methanol and ethanol in aqueous solutions at room temperature are 0.4–0.5 [11, 12]. In this case, Eq. (3) simplifies to

$$V(1:1\ \text{Adduct}) = \frac{V_1k_2\alpha lx}{k_2x^2 + (\alpha l + x)\sqrt{2k_5V_1}} \tag{4}$$

$$= \frac{V_1\alpha lx}{x^2 + (\alpha l + x)x_m^2/\alpha l_m}, \tag{4a}$$

where $k_2 = \alpha l_m\sqrt{2k_5V_1}/x_m^2$ is found from the root of quadratic equation derived from the condition $\partial V(1:1\ \text{Adduct})/\partial x = 0$, and x_m and l_m are the values of x and l at the maximum, respectively. For Eq. (4) with mole fractions instead of molar concentrations [equivalent to form (3a) at $\alpha = \gamma$] $k_2 = \{\alpha[(1/\chi_m) - 1]^2 - 1\}\sqrt{2k_5V_1}/(l+x)$, where χ_m is the value of $\chi = x/(l+x)$ at the maximum. At $k_{1b} = 0$, Eqs. (4) and (4a) determine the rate of reaction **3** alone.

Under conditions (i) $k_2x^2 \ll (\alpha l + x)\sqrt{2k_5V_1}$, $\alpha l \gg x$ and (ii) $k_2x^2 \gg (\alpha l + x)\sqrt{2k_5V_1}$, Eq. (4) transforms into simple relationships that allow parameters k_2 and α to be tentatively evaluated and describe the initial (ascending) and the final (descending) parts of the rate curve, respectively:

$$V(1:1\ \text{Adduct}) = \sqrt{V_1}k_2x/\sqrt{2k_5}, \tag{5}$$

$$V(1:1\ \text{Adduct}) = V_1\alpha l/\varphi x, \tag{6}$$

where $\varphi = 1$ for conditions (i) and (ii) or $\varphi = 2$ at the maximum when $k_2x^2 \cong (\alpha l + x)\sqrt{2K_5V_1}$.

Thus obtained versions (1), (3), (3a), (4) and (4a) of the rate equation[2] can be used to describe a variety of competing processes of unbranched-chain radical addition resulting in formation of small entities in binary systems with comparable concentration of the components. In particular, versions (4) and (4a) are applicable in describing liquid-phase processes of formation of organic hydroperoxides and alcohols upon oxidation of some hydrocarbons and their derivatives when the production of these compounds substantially exceeds that of carbonyl compounds.

A KINETIC MODEL FOR OXIDATION: OXYGEN AS AN AUTOINHIBITOR

In a kinetic model for oxidation of hydrocarbons yielding alkylperoxy radicals that are able to interact with molecular oxygen again (Scheme **II**), reaction **1b** of Scheme **I** is ignored ($l = [R_1A] \gg [R_2B] = x$, $k_{1b} = 0$, and $V_1 = V_{1a}$), $R_1A = RH$, $R_2B = O_2$, and $R_3^{\cdot} = RO_2^{\cdot}$. Dissociation reaction **1** of the initiator **I** gives some reactive radical R_0 which, being conversed into the final product R_0H, generates a hydrocarbon radical $R^{\cdot}$ involved in chain propagation. The addition of radical $R^{\cdot}$ to an oxygen molecule in reaction **2** gives rise to alkylperoxy radical adduct $RO_2^{\cdot}$, which forms, by chain propagation reaction **3**, alkylhydroperoxide $R_3A{=\!=}RO_2H$ (with regeneration of the chain-propagation radical $R^{\cdot}$) or alcohol ROH (with subsequent regeneration of the radical $R^{\cdot}$ in reaction **3b**). Reaction **3a** involves isomerization and degradation of the alkylperoxy adduct radical $RO_2^{\cdot}$ by cleavage of

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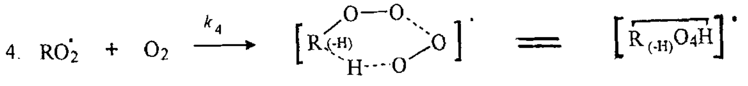
[2] Unlike the equation in Poluektov *et al.* [13], which is inapplicable to processes with competing reactions [3].

O—O and C—H bonds (or C—C bonds when the number of carbon atoms in a carbonyl compound and an alcohol produced in the chain process is less than that of the parent hydrocarbon) [14] and gives a carbonyl compound $R_{(-2H)}HO$ or $R'_{(-H)}HO$, and reaction **3b** gives water or alcohol R″OH (here the R′ and R″ radicals have a smaller number of carbon atoms as compared to $R^{\cdot}$). As follows from given Scheme **II** for the process occurring in the quasi-steady-state mode, reactions **3a** and **3b** (the latter involves the oxygen-containing fragment radicals $^{\cdot}OH$ and $R''O^{\cdot}$) have the identical rate and may be considered a united process that occurs in the solvent cage. We assume that reaction **4**, which is competitive to chain-propagation reactions **3** and **3a**, **3b**, gives the alkylhydrotetraoxy radical[3] [15] as the low reactivity radical $R_2^{\cdot}$ of Scheme **I** that inhibits the chain process and has the structure of a 6-membered cycle[4] or a 7-membered cycle as in the case of aromatic or certain branched acyclic hydrocarbons:



Reactions **6** and **7** of disproportionation of $R^{\cdot}$ and $[\overline{R_{(-H)}O_4H}]^{\cdot}$ radicals involve isomerization and degradation of the radical $[\overline{R_{(-H)}O_4H}]^{\cdot}$ accompanied by chemiluminescence observed upon oxidation of hydrocarbons [19]. These reactions result in recovery of molecular oxygen (presumably including singlet oxygen [19]), formation of carbonyl compound $R_{(-2H)}HO$ (presumably in triplet excited state [19]) and, depending on the degradation pathway, alcohol ROH, olefin $R_{(-2H)}H$ (in oxidation of a saturated hydrocarbon), hydrogen peroxide, and water. It is likely that isomerization and degradation of the radical

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[3] The thermochemistry of some polyoxy radicals [the enthalpy of formation is $\Delta H_f^0(CH_3O_4^{\cdot}) = 121.3 \pm 9\,kJ\,mol^{-1}$ by these data] and polyoxides [$\Delta H_f^0(CH_3O_4H) = -21.0 \pm 9\,kJ\,mol^{-1}$] is known [16], a number of physicochemical and geometrical parameters of the molecule have been calculated for methylhydrotetraoxide as a model compound [17–19], and IR spectra of dimethyltetraoxide with isotopically labeled groups have been measured in Ar + O_2 matrices [20].

[4] The cycle $[\overline{R_{(-H)}O_4(R)H}]^{\cdot}$ of the same six atoms (C, 4O, and H) with presumably hydrogen bonding H···O formed by recombination of primary and secondary alkylperoxy radicals $RO_2^{\cdot}$ according to the Russel mechanism [14].

$[\overline{R_{(-H)}O_4H}]^{\cdot}$ *via* reactions **6** and **7** can involve, as in the case of reaction **3a** for alkylperoxy radical $RO_2^{\cdot}$, the C—C bond rupture and formation of carbonyl compounds, alcohols, ethers, and organic peroxides, including those with a lesser number of carbon atoms than in the initial hydrocarbon. At higher conversions, the aldehydes formed can further be oxidized to the corresponding carboxylic acids.

I. Chain initiation

1. $I \xrightarrow{2k_1} R_0^{\cdot} + R_0^{\cdot}$

1a. $R_0^{\cdot} + RH \xrightarrow{k_{1a}} R_0H + R^{\cdot}$

II. Chain propagation

2. $R^{\cdot} + O_2 \xrightarrow{k_2} RO_2^{\cdot}$

3. $RO_2^{\cdot} + RH \xrightarrow{k_3} RO_2H + R^{\cdot}$

$(\text{or } ROH + RO^{\cdot})$

3a. $RO_2^{\cdot} \xrightarrow{k_{3a}} R_{(-2H)}HO + {}^{\cdot}OH$

$(\text{or } R'_{(-H)}HO + R''O^{\cdot})$

3b. ${}^{\cdot}OH + RH \xrightarrow{k_{3b}} H_2O + R^{\cdot}$

$(\text{or } R''O^{\cdot}(RO^{\cdot}) + RH \xrightarrow{k_{3b}} R''OH(ROH) + R^{\cdot})$

4. $ROz_2^{\cdot} + O_2 \xrightarrow{k_4} [\overline{R_{(-H)}O_4H}]^{\cdot}$

III. Chain termination

5. $R^{\cdot} + R^{\cdot} \xrightarrow{2k_5} RR$

$(\text{or } R_{(-2H)}H + RH)$

6. $R^{\cdot} + [\overline{R_{(-H)}O_4H}]^{\cdot} \xrightarrow{k_6} ROH + R_{(-2H)}HO + O_2$

$(\text{or } R_{(-2H)}H + R_{(-2H)}HO + H_2O + O_2)$

7. $[\overline{R_{(-H)}O_4H}]^{\cdot}\ [\overline{R_{(-H)}O_4H}]^{\cdot} \xrightarrow{2k_7} ROH + R_{(-2H)}HO + 3O_2$

$(\text{or } 2R_{(-2H)}HO + H_2O_2 + 2O_2)$

SCHEME **II**[5]

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[5] The kinetic model of oxidation given by Scheme **II** differs from that of chain addition process of α-hydroxyalkyl radicals to formaldehyde in alchohol–formaldehyde systems [2, 3] only in the lack of 1 : 1 adduct in reaction **4**.

Equations for rates of the elementary oxidation reactions as derived in terms of Scheme **II**[1] with parameters $\alpha = k_3/k_4$, $\beta = k_{3a}/k_4$ (mol L^{-1}), and $f = k_2x^2 + (\alpha l + \beta + x)\sqrt{2K_5V_1}$ are as follows:

$$V_3(\mathrm{ROOH, 2ROH}) = V_1k_2\alpha lx/f \tag{7}$$

$$= V_1\alpha lx/f_m, \tag{7a}$$

$$V_{3a}(\mathrm{R_{(-2H)}HO, R'_{(-H)}HO}) = V_{3b}(\mathrm{R''OH, H_2O}) = V_1k_2\beta x/f \tag{8}$$

$$= V_1\beta x/f_m, \tag{8a}$$

where $k_2 = (\alpha l_m + \beta)\sqrt{2k_5V_1}/x_m^2$ is found from the condition of extremum of the rate function $\partial V_{3,3a}/\partial x = 0$; x_m and l_m are the values of x and l at the maximum, respectively; and $f_m = x^2 + (\alpha l + \beta + x)x_m^2/(\alpha l_m + \beta)$;

$$V_5 = 2k_5V_1^2(\alpha l + \beta + x)^2/f^2, \tag{9}$$

$$2V_6 = 2V_1k_2x^2(\alpha l + \beta + x)\sqrt{2k_5V_1}/f^2, \tag{10}$$

$$V_7 = V_1k_1^2x^4/f^2. \tag{11}$$

Unlike the rates of reactions **4** (at $k_{1b} = 0$, $V_4 \leq V_1$), **5**, and **7** [Eqs. (9) and (11)]; the dependences of rates of reactions **3**, **3a** and **6** [Eqs. (7), (7a), (8), (8a) and (10)] on x pass through a maximum. The ratios of the rates of competing reactions are $V_3/V_4 = \alpha l/x$ and $V_{3a}/V_4 = \beta/x$ and those of chain propagation are $V_3/V_{3a} = \alpha l/\beta = k_3l/k_{3a}$ at a chain length given by $\nu = (V_3 + V_{3a})/V_1$. At $\alpha l \gg \beta$, Eqs. (7) and (7a) transform into (4) and (4a), respectively. For $k_2x^2 \gg (\alpha l + \beta + x)\sqrt{2k_5V_1}$ (descending part of the curve) Eqs. (7) and (8) become (6) and (12), respectively, thus expressing ordinary inversely proportional dependences on x and allowing parameters α and β to be tentatively evaluated:

$$V_{3a} = V_1\beta/\varphi x, \tag{12}$$

where $\varphi = 2$ at the maximum or $\varphi = 1$ otherwise.

In the alternative kinetic model for oxidation when $RO_2^{\cdot}$ rather than $R^{\cdot}$ radicals take part in reactions with each other and radicals $[\overline{R_{(-H)}O_4H}]^{\cdot}$ at the chain termination stage of Scheme **II**, dependences of the rate of chain formation of products on oxygen concentration x, as derived in the same fashion[1], have no maximum: $V_3 = V_1k_3l/(k_4x + \sqrt{2k_5V_1})$ and $V_{3a} = V_1k_{3a}(k_4x + \sqrt{2k_5V_1})$. In the kinetic model of oxidation, in which competitive reaction **4** is lacking ($k_4 = 0$) and radicals $R^{\cdot}$ and $RO_2^{\cdot}$ (the latter is used instead of $[\overline{R_{(-H)}O_4H}]^{\cdot}$ in Scheme **II**) take part in reactions 5–7 of three types of quadratic chain termination (Scheme **II**), the functions V_3 and V_{3a} derived in the same manner are also fractional rational functions of the type $a_0x/(b_0x + c_0)$ having no maximum, where a_0, b_0, and c_0 are coefficients. For such a kinetic model that does not include reactions **3a**, **3b** and **4** of Scheme **II** (k_{3a}, $k_4 = 0$), the dependence of the rate $V_2 = V_3$ on component concentration x obtained by the quasi-steady-state approximation [1] on the assumption of sufficiently large chain lengths when it is possible that $V_2 = V_3$ and without substitution $k_6 = \sqrt{2k_52k_7}$ as in this work is an irrational function $a_1x/(b_1x^2 + c_1x + d_1)^{1/2}$ ($a_1 - d_1$ are coefficients) and also has no maximum with varying concentration of any of the two components.

Thus, the two latter models out of the three kinetic oxidation models involving adduct radicals $RO_2^{\cdot}$ in the chain propagation step, which we analyzed mathematically, are the versions of the generally accepted model [1, 14] and result in the plot of dependence of oxidation rate upon oxygen concentration in the form of a curve arising from the origin of coordinates, being convex upwards, and having the asymptote parallel to the *abscissa*. Dependences of this sort are observed experimentally under the conditions of limited oxygen solubility in a given liquid when the attained concentration of oxygen is $[O_2]_{top} \le x_m$[6]. Unlike the generally accepted model, the kinetic model that includes reaction **4** competing with chain propagation reactions **3** and **3a**, **3b** (Scheme **II**) makes it possible to describe the nonmonotontic (with

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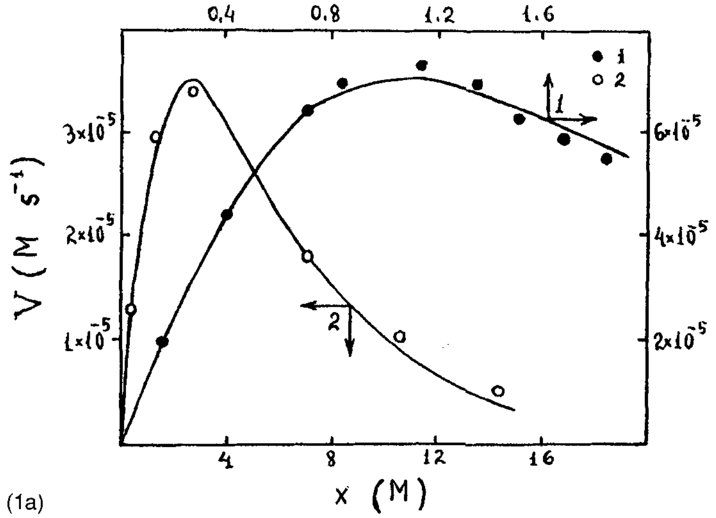
[6] The practical solubility of oxygen in a liquid is not necessarily equal to its calculated equilibrium thermodynamic concentration because of diffusional constraints, which retard the establishment of gas–liquid saturated solution equilibrium under given experimental conditions (for example, upon gas bubbling through the liquid) or because of disobedience of the Henry law for a particular gas–liquid system under real conditions.

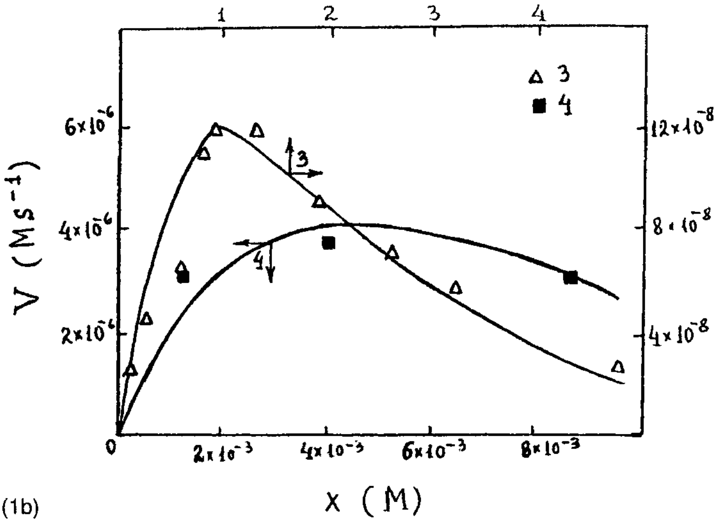
maximum) dependence of oxidation rate on oxygen concentration (Fig. 1b, curve 4). By this oxidation model, as oxygen concentration in the binary system increases, it begins to act as an autoinhibitor of the oxidation process (reactions **4** and **6**) and its optimum concentration x_m can be calculated by means of the derived rate Eqs. (7a), (8a) and (4a).

In should be pointed out that the application of the competition kinetics to the oxidation of hydrogen according to Scheme **II** [R = H, k_{3a}, $k_{3b} = 0$, Eqs. (4) and (4a)] implies that the formation of $HO_2^{\cdot}$, H_2O_2, $HO_4^{\cdot}$ and H_2O_4 species; the existence of the two latter was



(1a)

FIGURE 1 Reconstruction of the functional dependence of the reaction rate V(1 : 1 Adduct) on the initial concentration x of unsaturated component (or oxygen) from experimental data for systems: (1) CCl_4-2-methyl-1-propene at 378 K, $V_1 = 2.6\times10^{-7}$ M s^{-1} [6], $\alpha = 65 \pm 10$ as found by optimizing the model in parameter α [Eq. (4a)], the corresponding calculated rate constant $k_2 = (4.3 \pm 0.9)\times10^{3}$ M^{-1}s^{-1}, and standard deviation for approximation of the function $S_Y = 3.87\times10^{-6}$; (2) PCl_3-2-methyl-1-propene at 303 K, $V_1 = 4.65\times10^{-9}$ M s^{-1} [5], $\alpha = (6.7 \pm 1)\times10^{3}$, $k_2 = (6.9 \pm 1.4)\times10^{3}$ M^{-1}s^{-1}, and $S_Y = 2.37\times10^{-6}$; (3) C_2H_5Br-1-octene at 343 K, $V_1 = 2.6\times10^{-7}$ M s^{-1} [7], $\alpha = (1.3 \pm 0.2)\times10^{-1}$, $k_2 = (1.4 \pm 0.3)\times10^{2}$ M^{-1}s^{-1}, and $S_Y = 1.95\times10^{-8}$; and (4) *ortho*-xylene-O_2 at 373 K, $V_1 = 4.73\times10^{-7}$ M s^{-1} [15] (the initiation yield $G_i = 2.6$ species/100 eV [25], dose rate $P = 2.18$ Gy s^{-1}, and oxygen concentration as calculated by its solubility data in xylene [26]), $\alpha l \gg \beta$, $\alpha = (9.0 \pm 1.8)\times10^{-3}$, $k_2 = (3.2 \pm 0.8)\times10^{5}$ M^{-1}s^{-1}, and $S_Y = 5.37\times10^{-7}$. The 1 : 1 adducts (two isomers each) formed *via* chain mechanism in reaction **3** of chain propagation are: (1) $Cl_3CCH_2CCl(CH_3)CH_3$, (2) $Cl_2PCH_2CCl(CH_3)CH_3$, (3) $C_2H_5CH_2CHBr(CH_2)_5CH_3$ and (4) $CH_3C_6H_4CH_2O_2H$.



(1b)

FIGURE 1 (Continued).

proved by UV and IR spectroscopy, respectively, in Staehelin *et al.* [21] and Yagodovskaya *et al.* [22] (by the data [16], the enthalpy of formation ΔH_f^0 of these species is 12.6 ± 1.7, -136.0 ± 0, 122.6 ± 8, and $-26.0 \pm 9\,\mathrm{kJ\,mol^{-1}}$). The structure of hydrotetraoxy radical $HO_4^{\cdot}$ produced in reaction **4** may also be represented in the form of hydrogen-bonded cycle $[\overline{\mathrm{OO}\ldots\mathrm{H}\ldots\mathrm{OO}}]^{\cdot}$ [23].

EXAMPLES OF KINETIC DESCRIPTION OF EXPERIMENTAL RATE CURVES

Figures 1a and 1b show the kinetic curves calculated by Eq. (4a) to fit particular experimental dependences of the formation rate of 1 : 1 adducts on concentration of the unsaturated component (or oxygen) in CCl_4 (or PCl_3)-2-methyl-1-propene [5, 6], C_2H_5Br-1-octene [7], and *ortho*-xylene-O_2 [15] binary systems.

In regard to the latter system, the available published data on the dependence of rate of radical chain formation of some oxidation product on concentration of dissolved oxygen in liquid phase are insufficient. Therefore, this work is limited to the only available example of radiation-induced oxidation of *ortho*-xylene [15]. In that case, the yield of *ortho*-xylene hydroperoxide at 373 K substantially exceeds that of *ortho*-toluic aldehyde, *i.e.*, $\alpha l \gg \beta$, which makes it possible to use Eq. (4a) with the single adjustable parameter α to describe the experimental rate dependence; the limitation of oxygen solubility in *ortho*-xylene is attained at a concentration $[O_2]_{top} > x_m$, corresponding to the third experimental data point (Fig. 1b, curve 4).

Note that, when the of R_1—A bond energy of the saturated component is not higher but approximately equal to or lower than the R_2—B bond energy of the unsaturated component, a relative rate of reaction **4** with respect to competing chain propagation reaction **3** appears sufficient for successful application of the rate equation in forms (1), (3), (3a), (4), and (4a) to describe the 1 : 1 adduct formation in these reaction systems at high temperatures alone [6]. For example, in the case of the PCl_3-1-propene system, the difference in energy between the R_2—B and R_1—A bonds (where B and A are the hydrogen and halogen atoms, respectively) in the gas phase at 298 K [24] is as small as 5 kJ mol^{-1}, whereas that for the CCl_4-2-methyl-1-propene (or cyclohexene) and C_2H_5Br-2-methyl-2-butene systems is 20.9 (or 37.7) and about 24 kJ mol^{-1}, respectively.

Acknowledgements

The author is grateful to Professor Lenar T. Bugaenko and Professor Alexander Ya. Rozovskii for the useful discussions and to Mr. Yuri E. Gorbachev (Dialogue-INFO Joint Stock Company) for the financial support.

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