

CHEMICAL KINETICS AND CATALYSIS

The Competition Kinetics of Radical-Chain Addition

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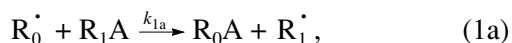
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Abstract—A scheme of reactions involving radicals of three types, one of which inhibits the chain process, is suggested and used to derive kinetic equations with one to three parameters that should be determined experimentally. The equations describe a nonmonotonic (with a maximum) dependence of the rate of the addition of a free radical to a double bond with the formation of a 1 : 1 adduct on the concentration of the unsaturated compound; they apply to unbranched chain processes in liquid homogeneous binary mixtures comprising saturated (hydrocarbon, alcohol, etc.) and unsaturated (olefin, formaldehyde, or molecular oxygen) components.

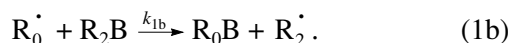
Chain unbranched reactions of the addition of free radicals to double bonds with the formation of small molecules (1 : 1 adducts) are usually described by reaction schemes with radicals of two types, *viz.*, radicals involved in chain propagation (addends) and addition radicals (adducts) [1]. The resulting kinetic equations describe monotonic reaction rate dependences on the concentration of unsaturated components. In this work, we use a scheme according to which the reaction competing with the chain propagation reaction produces radicals of the third type. These radicals inhibit the chain process by causing decay of chain-leading radicals. Based on this scheme and using the method of quasi-stationary concentrations, we derived kinetic equations with one to three parameters that should be experimentally determined. These equations describe nonmonotonic (with maxima) dependences of the rate of the formation of 1 : 1 adducts on the concentration of the unsaturated component for a wide variety of radical-chain unbranched reactions. These are kinetically competitive radical-chain unbranched processes of the addition of free radicals from saturated to unsaturated components in liquid homogeneous binary systems.

The general scheme of unbranched chain processes of the addition of free radicals from a saturated compound to an olefin (and its functional derivatives), formaldehyde, or oxygen in binary systems comprising reaction participants has the following form:

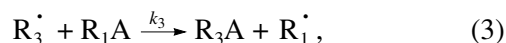
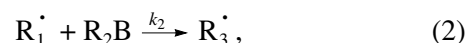
Chain initiation:



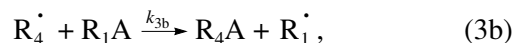
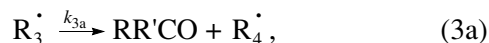
for the addition to an olefin at commensurate component concentrations



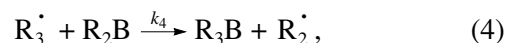
Chain propagation:



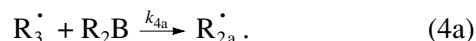
for the addition of O₂ and α-hydroxyalkyl radical to CH₂O



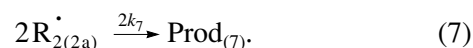
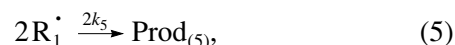
for the addition to an olefin and CH₂O



for the addition to O₂



Chain termination:

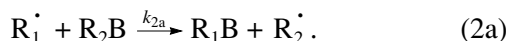


In this scheme, I is the initiator such as peroxide [1–3]; R₀[·] is some active radical; A is hydrogen [1–6] or halogen [7–9]; B is hydrogen [1–5, 7–9], halogen [6], or oxygen (in oxidation) [10]; R₁[·] is a $\dot{P}Cl_2$ - [7] or $\dot{C}Cl_3$ -type [8] radical, a saturated hydrocarbon radical [1, 9], or an α-hydroxyalkyl [1–6] or similar functionally substituted radical [1] (radical-addend); R₂[·] is the oxygen atom (in oxidation) [10], the formyl radical [3–5], an unsaturated hydrocarbon (starting with propenyl) radical [1, 2, 6–9], or an α-hydroxyalkenyl [2, 4, 5] or similar functionally substituted radical [1]; R_{2a}[·] is a cycloalkylhydrotetraoxyl radical $[R_{(-H)}O_4H]^{\cdot}$; R₃[·] is

the radical-adduct [1–10]; R_4^\cdot is the hydroxymethyl [3–5], hydroxyl, or alkoxy (in oxidation) [10] radical; R_0A , R_0B , R_1A , and R_4A are saturated compounds; R_2B is an unsaturated compound; $RR'CO$ is a carbonyl compound [3–5]; R_3A and R_3B are final (nonradical) products (1 : 1 adducts); and Prod are final radical recombination or disproportionation products.

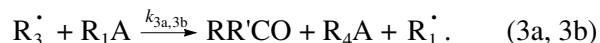
The addition to olefins is described by reactions (1), (1a), (1b), (2), (3), (4), and (5)–(7); to the carbon atom of the carbonyl group of the free (unsolvated) formaldehyde form,¹ by reactions (1), (1a), (2), (3), (3a), (3b), (4), and (5)–(7); and to molecular oxygen, by reactions (1), (1a), (2), (3), (3a), (3b), (4a), and (5)–(7). The scheme includes three pairs of parallel competing reactions: (1a) and (1b), (3) and (4) [or (4a)], and (3a) and (4) [or (4a)].

In parallel with reaction (2), reaction (2a) may occur:

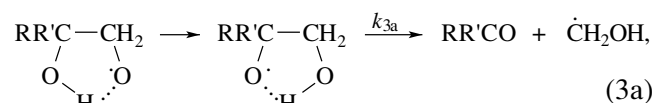


This reaction does not play any significant role in chain propagation and is not necessary for a kinetic description of the process because the rate ratio $V_2/V_{2a} = k_2/k_{2a}$ between these reactions is independent of the concentration of unsaturated component R_2B . Some other possible radical-molecular reactions were shown in [4] to have low probabilities. The heaviest radical-adduct R_3^\cdot formed in reaction (2) can possess enhanced energy because of the difference in energy released when the double bond becomes single [13]. This radical can therefore abstract the least strongly bound atom A or B from neighboring R_1A or R_2B component molecules even within a matrix cage without diffusing outside it.

According to the suggested scheme of the process occurring under quasi-stationary conditions, reaction (1) of chain initiation occurs as a result of the decomposition of chemical initiators [1–3] or under the action of light [1, 2] or ionizing radiation [4–10] at a rate $V_1 = V_{1a} + V_{1b}$. Similarly, reactions (3a) and (3b) ($V_{3a} = V_{3b}$) involving fragmentation-type radicals R_4^\cdot can be treated as one chain propagation reaction occurring in a solvate cage,



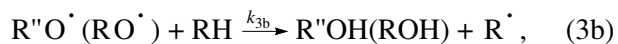
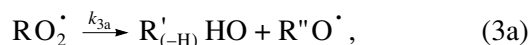
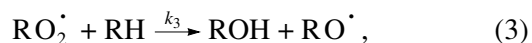
For the addition of the α -hydroxyalkyl radical ($R_1^\cdot = RR'\dot{C}OH$) to formaldehyde, the mechanism of reaction (3a) can be represented as [4, 5]



¹ The concentration of this form in solution exponentially grows with temperature [11]. The concentration of the solvent in solutions of formaldehyde can be estimated as described in [12].

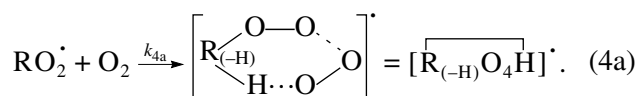
where $R_3^\cdot = RR'C(OH)CH_2O^\cdot$, $R_4^\cdot = \dot{C}H_2OH$, and $RR'CO$ is a carbonyl compound.

In processes of addition to oxygen, reactions (3), (3a), and (3b) can go in an alternative direction to produce alcohols, possibly with a smaller number of carbon atoms in radicals R' and R'' than in the initial hydrocarbon radical R :



where $R_1A = RH$, $R_3^\cdot = RO_2^\cdot$ and ROH , $R_4A = R''OH$ (alcohols) and $R'_{(-H)}HO$ (carbonyl compound).

In chain initiation by reaction (1b) competing with (1a) and chain propagation by reaction (4) or (4a) competing with (3) and (3a, 3b), a low-activity (for instance, because of resonance stabilization [13]) radical R_2^\cdot or R_{2a}^\cdot is formed; this radical inhibits the chain process of the addition at the step of quadratic chain termination as a result of cross combination with chain-leading radical R_1^\cdot by reaction (6). If radical-adduct R_3^\cdot undergoes addition to molecular oxygen by reaction (4a), the role of low-activity radical R_{2a}^\cdot may be played by an alkylhydrotetraoxyl radical [10] of a cyclic structure with a six-² or seven-membered ring (seven-membered rings are formed from aromatic or some branched acyclic hydrocarbons):



Frequently observed monotonic dependences of the rate of oxidation on the partial pressure of oxygen (with kinetic curves reaching a plateau [1, 14]) are explained by limited oxygen solubilities in liquids under reaction conditions with diffusion limitations (for instance, when oxygen is bubbled through a liquid) and by deviations from the Henry law if the attained concentration of oxygen in a liquid is lower than its thermodynamically equilibrium concentration.

1 : 1 Adducts are formed in chain-propagation reactions (3) and (3a, 3b) (the main chain-process products are R_3A , $RR'CO$, and R_4A) and in competing reaction (4) inhibiting chain propagation (the side "nonchain"

² The $R_{(-H)}O_4(R)H$ ring of the same six atoms (C, 4O, and H) with a supposed $H \cdots O$ hydrogen bond is also formed in recombination of primary and secondary alkylperoxyl radicals RO_2^\cdot by the Russell mechanism [14]. The thermochemistry of some polyoxyl radicals and polyoxides is considered in [15].

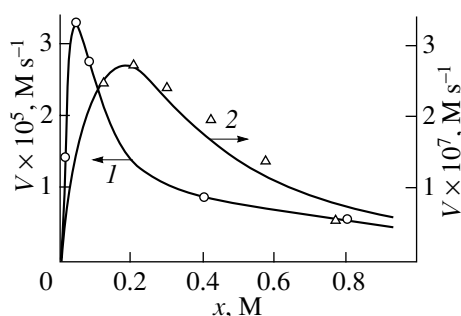


Fig. 1. Reproduction of functional dependences by equations (I) and (II) from experimental data on the systems: (1) 2-propanol-2-propene-1-ol (433 K, $V_1 = 3.18 \times 10^{-6} \text{ M s}^{-1}$, $2k_5 = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, product $\text{CH}_3(\text{CH}_3)\text{C}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ [4, 5], equation (I): $\alpha = (6.8 \pm 0.8) \times 10^{-2}$, $k_2 = (1.0 \pm 0.14) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, standard deviation of the approximation function $s_Y = 5.91 \times 10^{-7}$) and (2) 1-propanol- CH_2O (413 K, $V_1 = 4.07 \times 10^{-7} \text{ M s}^{-1}$, $2k_5 = 4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, product $\text{CH}_3\text{CH}_2\text{CHO}$ [4], equation (II): $\alpha = 0.36 \pm 0.07$, $\beta = 0.25 \pm 0.05 \text{ M}$, $k_2 = (6.0 \pm 1.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, $s_Y = 2.38 \times 10^{-8}$).

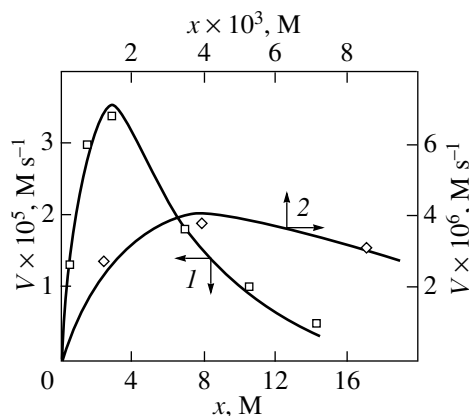


Fig. 2. Reproduction of functional dependences by equation (IIIa) (at $\beta = 0$) from experimental data on the systems: (1) PCl_3 -2-methyl-1-propene (303 K, $V_1 = 4.65 \times 10^{-9} \text{ M s}^{-1}$, $2k_5 = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, product $\text{Cl}_2\text{PCH}_2(\text{Cl})\text{C}(\text{CH}_3)\text{CH}_3$ [7], $\alpha = (6.7 \pm 1) \times 10^{-3}$, $k_2 = (6.9 \pm 1.4) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$, standard deviation of the approximation function $s_Y = 2.37 \times 10^{-6}$) and (2) *o*-xylene- O_2 (373 K, $V_1 = 4.73 \times 10^{-7} \text{ M s}^{-1}$, $2k_5 = 1.15 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, concentration of oxygen was calculated from its solubility in xylene [23], product $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{O}_2\text{H}$ [10], $\alpha l \gg \beta$, $\alpha = (9.0 \pm 1.8) \times 10^{-3}$, $k_2 = (3.2 \pm 0.8) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$, $s_Y = 5.37 \times 10^{-7}$).

product is R_3B). The rate of the formation of 1 : 1 adducts is a complex function of the rates of formation and decay of radicals R_1 and $\text{R}_{2(2a)}$:

$$V(\text{R}_3\text{A}, \text{R}_3\text{B}, \text{RR}'\text{CO}, \text{R}_4\text{A}) = V_2 = V_3 + V_{3a, 3b} + V_4 \\ = (V_{1a} + V_3 + V_{3a, 3b} - V_5) - (V_{1b} + V_{4(4a)} - V_7).$$

The reaction scheme suggested above was used to derive³ equations for the rates of formation of various final products in a binary reaction mixture under the conditions of the presence of the saturated component in excess over the unsaturated reaction participant ($[\text{R}_1\text{A}] \gg [\text{R}_2\text{B}]$, $k_{1b} = 0$); these equations describe reaction rates as depending on the nature of the unsaturated compound.

If the unsaturated component is formaldehyde ($k_{4a} = 0$) or olefin ($k_{3a} = k_{4a} = 0$, $\beta = 0$), then

$$V(\text{R}_3\text{A}, \text{R}_3\text{B}) = V_3 + V_4 \\ = \frac{V_1 k_2 (\alpha l + x)x}{k_2 x^2 + (\alpha l + \beta + x)(2k_5 V_1)^{1/2}}, \quad (\text{I})$$

where $l = [\text{R}_1\text{A}]$ and $x = [\text{R}_2\text{B}]$ are the initial molar concentrations of the initial compounds; k_2 is the rate constant for the addition of free radical R_1^\cdot from saturated component R_1A to unsaturated component R_2B ; and $\alpha = k_3/k_{4(4a)}$ and $\beta = k_{3a}/k_{4(4a)}$, mol/l, are the ratios between the rate constants for competing reactions. If the reaction is the addition to formaldehyde, then the products formed in reactions (3) and (4) in saturated alcohol-formaldehyde systems are α -diols ($\text{R}_3\text{A} = \text{R}_3\text{B} = \text{R}_3\text{H}$) [4, 5]. If the addition to an olefin occurs, then $\beta = 0$ in (I), and the condition of the extremum of the rate function, $\partial V/\partial x = 0$, yields $k_2 = [(\alpha l_m)^{1/2}/x_m + 1/(\alpha l_m)^{1/2}]^2 (2k_5 V_1)^{1/2}$, where x_m and l_m are the x and l values at the maximum. In saturated alcohol-2-propene-1-ol systems, the products are γ -diols ($\text{R}_3\text{A} = \text{R}_3\text{B} = \text{R}_3\text{H}$) [4, 5].

If the unsaturated component is formaldehyde ($k_{4a} = 0$) or molecular oxygen ($\text{R}_2\text{B} = \text{O}_2$, $k_4 = 0$), then

$$V(\text{RR}'\text{CO}, \text{R}_4\text{A}) = V_{3a} = V_{3b} \\ = \frac{V_1 k_2 \beta x}{k_2 x^2 + (\alpha l + \beta + x)(2k_5 V_1)^{1/2}} \quad (\text{II})$$

$$= \frac{V_1 \beta x}{x^2 + (\alpha l + \beta + x)x_m^2/(\alpha l_m + \beta)}, \quad (\text{IIa})$$

where $k_2 = (\alpha l_m + \beta)(2k_5 V_1)^{1/2}/x_m^2$. In saturated alcohol-formaldehyde systems, the products formed in reactions (3a) and (3b) are a carbonyl compound ($\text{RR}'\text{CO}$) and methanol (R_4A) [4, 5]. In hydrocarbon-molecular oxygen systems, the products formed in

³ The derivation was performed by the method of quasi-stationary concentrations, which allows the exponent of the $2k_5[\text{R}_1^\cdot]^2$ term in the equation $d[\text{R}_1^\cdot]/dt = 0$ to be decreased from 2 to 1 [4]: $k_6 = (2k_5 2k_7)^{1/2}$ and $V_1 = V_5 + 2V_6 + V_7 = \{(2k_5)^{1/2}[\text{R}_1^\cdot] + (2k_7)^{1/2}[\text{R}_2^\cdot]\}^2$.

reactions (3a) and (3b) are carbonyl compounds $RR'CO$, which may contain fewer carbon atoms than the initial hydrocarbon, an alcohol R_4A with a smaller number of carbon atoms in comparison with the initial hydrocarbon, and water ($R_4 = OH$, $A = H$) [10].

If the unsaturated component is molecular oxygen ($R_2B = O_2$, $k_4 = 0$) or if the concentration of the saturated component is insignificantly higher than that of the olefin ($k_{3a} = k_{4a} = 0$, $\beta = 0$), that is, at commensurate component concentrations ($[R_1A] > [R_2B]$, $k_{1b} \neq 0$), and if the condition $k_{1a}/k_{1b} \approx k_3/k_4$ is satisfied,⁴ then

$$\begin{aligned} V(R_3A, R_3B) &= V_3 + V_4 \\ &= \frac{V_1 k_2 \alpha l x}{k_2 x^2 + (\alpha l + \beta + x)(2k_5 V_1)^{1/2}} \quad (\text{III}) \\ &= \frac{V_1 \alpha l x}{x^2 + (\alpha l + \beta + x)x_m^2/(\alpha l_m + \beta)}, \quad (\text{IIIa}) \end{aligned}$$

where $k_2 = (\alpha l_m + \beta)(2k_5 V_1)^{1/2}/x_m^2$. In hydrocarbon-molecular oxygen systems, the products formed in reaction (3) are an alkylhydroperoxide (R_3A) and an alcohol [10]. If the yield of these products is substantially higher than the yields of carbonyl compounds in oxidation of hydrocarbons ($\alpha l \gg \beta$) and hydrogen⁵ ($R_1A = H_2$, $k_{3a} = 0$) [18–20], and if the addition to an olefin occurs, then $\beta = 0$ in the expression for k_2 and equations (III) and (IIIa) [for the addition to an olefin at $k_{1b} = 0$, equations (III) and (IIIa) only determine rate $V_3(R_3A)$].

If the unsaturated component is an olefin ($k_{3a} = k_{4a} = 0$, $\beta = 0$, and, in addition, $k_{1b} = 0$), formaldehyde ($k_{4a} = 0$), or molecular oxygen ($R_2B = O_2$, $k_4 = 0$), the equations for the rates of formation of final products at the chain termination step are

$$V_5 = 2k_5 V_1^2 (\alpha l + \beta + x)^2 / f^2, \quad (\text{IV})$$

$$2V_6 = 2V_1 k_2 x^2 (\alpha l + \beta + x)(2k_5 V_1)^{1/2} / f^2, \quad (\text{V})$$

$$V_7 = V_1 k_2^2 x^4 / f^2, \quad (\text{VI})$$

⁴ For instance, rate constant ratios between reactions of various radicals (\dot{OH} , $CH_3O\dot{O}$, \dot{CH}_3 , $NO_3\dot{O}$, $H_2PO_4\dot{O}$) with methanol and ethanol at room temperatures are 0.4–0.5 [16, 17].

⁵ Note that, according to the scheme of reactions, $HO_2\dot{O}$, H_2O_2 , $HO_4\dot{O}$, and H_2O_4 species should then be formed in reactions (2), (3), (4a), and (6) and (7), respectively (with subsequent decay $H_2O_4 \longrightarrow H_2O_2 + O_2$). That the $HO_4\dot{O}$ and H_2O_4 particles do exist follows from their UV (294 K) and IR (77 K) spectra obtained in [18] and [19], respectively. The $HO_4\dot{O}$ hydrotetraoxyl radical has the structure of the $[OO\cdots H\cdots OO]\dot{O}$ ring with an H-bond [21].

where $f = k_2 x^2 + (\alpha l + \beta + x)(2k_5 V_1)^{1/2}$. For the addition to olefins, $\beta = 0$ in equations (IV)–(VI) and the expression for f .

If $k_2 x^2 \gg (\alpha l + \beta + x)(2k_5 V_1)^{1/2}$ (the descending branch of the kinetic dependence passing a maximum), equations (III) and (II) become simple functions describing the inversely proportional dependence of V on x , which can be used to preliminarily estimate the α and β parameters:

$$V(R_3A, R_3B) = V_1 \alpha l / \phi x, \quad (\text{VII})$$

$$V(RR'CO, R_4A) = V_1 \beta / \phi x, \quad (\text{VIII})$$

where $\phi = 2$ at the maximum [when $k_2 x^2 \approx (\alpha l + \beta + x)(2k_5 V_1)^{1/2}$], and $\phi = 1$ at the other points.

The ratios between the rates of competing reactions are $V_3/V_{4(4a)} = \alpha l/x$ and $V_{3a}/V_{4(4a)} = \beta/x$, and the chain length is $\nu = (V_3 + V_{3a})/V_1$. Unlike the rates of reactions (4a) or (4) at $k_{1b} = 0$ (with $V_{4(4a)} \leq V_1$) and the rates of reactions (5) and (7) [equations (IV) and (VI)], rates V of reactions (3), (3a), and (6) [equations (I)–(III) and (V)] pass maxima with x variations. The mathematical analysis [4] shows that the participation of radicals $R_2\dot{O}$ (or $R_2\dot{a}$) rather than radical-adducts $R_3\dot{O}$ [1] in reactions with each other and with radicals $R_1\dot{O}$ at the chain termination step ensures passage through a maximum of the rate of formation of 1 : 1 adducts with changes in the concentration of the unsaturated component. The maximum of the dependence described by (I)–(III) owes its existence to reactions (4) [or (4a)] competing with chain propagation reactions (3) and (3a).

The results of a kinetic description by (I)–(III) of the experimental data on the rates of formation of 1 : 1 adducts as functions of the concentration of unsaturated components in the 2-propanol–2-propene–1-ol [4, 5], 1-propanol–formaldehyde [4], PCl_3 –2-methyl-1-propene [7], and *o*-xylene– O_2 [10] binary systems are presented in Figs. 1 and 2.

Note that, if the energy of the R_1 – A bond in the saturated component is not higher than the dissociation energy of the R_2 – B bond in the unsaturated component, then the rate of reaction (4) relative to the rate of competing chain propagation reaction (3) is only sufficient at high temperatures for successfully applying kinetic equations (I)–(III) to describe the formation of 1 : 1 adducts [9]. For instance, in the PCl_3 –1-propene system, the difference between the dissociation energy of bonds R_2 – B (where B is hydrogen) and R_1 – A (where A is a halogen) in the gas phase at 298 K [22] is insignificant (5 kJ/mol), whereas in the CCl_4 –2-methyl-1-propene (or cyclohexene) and C_2H_5Br –2-methyl-2-butene systems, this difference amounts to 20.9 (or 37.7) and ~24 kJ/mol, respectively.

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