The Role of Competing Reactions in Kinetics of Nonbranched-Chain Addition Processes of Free Radicals to Alkenes and Their Derivatives

Michael M. Silaev

Abstract: The reaction scheme is suggested for the initiated nonbranched-chain addition of free radicals to the double bonds of the unsaturated compounds. The proposed scheme includes the reaction competing with chain propagation reactions through a reactive free radical. The chain evolution stage in this scheme involves three types of free radicals. One of them is relatively low-reactive and inhibits the chain process by shortening of the kinetic chain length. Based on the suggested scheme, four rate equations (containing one to three parameters to be determined directly) are deduced using quasi-steady-state treatment. These equations provide good fits for the nonmonotonic (peaking) dependences of the formation rates of the molecular products (1:1 adducts) on the concentration of the unsaturated component in binary systems consisting of a saturated component (hydrocarbon, alcohol, etc.) and an unsaturated component (alkene, allyl alcohol, etc.). The unsaturated compound in these systems is both a reactant and an autoinhibitor generating low-reactive free radicals. The energetics of the key radical-molecule reactions is considered.

Keywords: Low-Reactive Radical, Autoinhibitor, Competing Reaction, Kinetic Equation, Energy.

I. INTRODUCTION

A free radical may be low-reactive if its unpaired p-electron may be delocalized, e.g., over conjugated bonds as in the case of allyl radical $CH_2=CH\dot{C}H_2$.[1] In nonbranched-chain processes of reactive free radical (addend) addition to double bonds of molecules, the formation of rather low-reactive free radicals in reactions, which are parallel to or competing with propagation via a reactive radicals, lead to chain termination, because these low-reactive radicals (inhibitors) do not participate in further chain propagation and because they decay when colliding with each other or with chain-carrier reactive radicals thus resulting in inefficient expenditure of the latter and process inhibition.

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[1]Note that the activity of a free radical is also connected to the reaction heat in which it participates.

In similar processes involving the addend and inhibitor radicals in diffusion controlled bimolecular chain-termination reactions of three types, the dependences of the rate of molecular 1:1 adduct formation on the concentration of the unsaturated component (which is the source of low-reactive free radicals in a binary system of saturated and unsaturated components) have a maximum, usually in the region of small (optimal) concentrations.

Here, reactions of addition of reactive free radicals to double bonds of alkene and their derivatives to give 1:1 adduct radicals are taken as examples to consider the role of low-reactive free radicals as inhibitors of the nonbranched chain processes at moderate temperatures.

The 1:1 adduct radical (which is the heaviest and the largest among the free radicals that result from the addition of one addend radical to the double bond of the molecule) may have an increased energy owing to the energy liberated in the transformation of a double bond into an ordinary bond (30–130 kJ mol^{-1} for the gas phase under standard conditions [1–4]). Therefore, it can decompose or react with one of the surrounding molecules in the place of its formation without diffusing in the solution and, hence, without participating in radical-radical chain termination reactions. Which of the two reactions of the adduct radical, the reaction with the saturated component or the reaction with the unsaturated component, dominates the kinetics of the process will depend on the reactivity and concentration ratios of the components in the binary system.

Earlier [5, 6], there were attempts to describe such peaking dependences fragmentarily, assuming that the saturated or unsaturated component is in excess, in terms of the direct and inverse proportionalities, respectively, that result from the simplification of a particular case of the kinetic equation set up by the quasi-steady-state treatment of binary copolymerization involving fairly long chains [5]. This specific equation is based on an irrational function, whose plot is a monotonic curve representing the dependence of the product formation rate on the concentration of the unsaturated component. This curve comes out of the origin of coordinates, is convex upward, and has an asymptote parallel to the abscissa axis. Replacing the component concentrations with the corresponding mole fractions generates a peak in this irrational function and thereby makes it suitable to describe the experimental data [7]. However, this

circumstance cannot serve as a sufficient validation criterion for the mechanism examined, because the new property imparted to the function by the above artificial transformation does not follow from the solution of the set of algebraic equations that are set up for the reaction scheme accepted for the process in a closed system and express the equality of the steady-state formation and disappearance rates of the reactive intermediates.

This publication presents free radical additions to alkenes and their derivatives [8–11] yielding various 1:1 molecular adducts, whose formation rates as a function of the unsaturated compound concentration pass through a maximum. In the kinetic description of these nontelomerization chain processes, the reaction between the 1:1 adduct radical and the unsaturated molecule, which is in competition with chain propagation through a reactive free radical ($\cdot$PCl$_2$, C$_2$H$_5\dot{C}$HOH, etc.), is included for the first time in the chain propagation stage. This reaction yields a low-reactive radical (such as CH$_2$=C(CH$_3$)$\dot{C}$H$_2$) and thus leads to chain termination because this radical does not continue the chain and thereby inhibits the chain process [10]. We will consider kinetic variants for the case of comparable component concentrations with an excess of the saturated component [8, 9] and the case of an overwhelming excess of the saturated component over the unsaturated component [10, 11]. Based on the reaction scheme suggested for the kinetic description of the addition process, we have derived kinetic equations with one to three parameters to be determined directly.

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 build-up of the statistical error in the nonlinear estimation of these parameters in the case of a limited number of experimental data points [12]. The rate constant of the addition of a free radical to the double bond of the unsaturated molecule, 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.

The kinetic equations were set up using the quasi-steady-state treatment. This method is the most suitable for processes that include eight to ten or more reactions and four to six different free radicals and are described by curves based on no more than three to seven experimental points. In order to reduce the exponent of the $2k_5[R_1^\bullet]^2$ term in the $d[R_1^\bullet]/dt = 0$ equation to unity[8], we used the following condition for the early stages of the process: $k_6 = \sqrt{2k_5 2k_7}$ [16] and, hence, $V_1 = V_5 + 2V_6 + V_7 = (\sqrt{2k_5}[R_1^\bullet] + \sqrt{2k_7}[R_2^\bullet])^2$. Here, $[R_1^\bullet]$ and $[R_2^\bullet]$ are the concentrations of the addend radical and the low-reactive (inhibitor) radical, respectively; V_1 is the initiation rate; V_5, $2V_6$, and V_7 are the rates of the three types of diffusion-controlled quadratic-law chain termination reactions; $2k_5$ and $2k_7$ are the rate constants of the loss of identical free radicals via the reactions $R_1^\bullet + R_1^\bullet$ and $R_2^\bullet$

+ $R_2^\bullet$, respectively; k_6 is the rate constant of the loss of different free radicals via the $R_1^\bullet + R_2^\bullet$ reaction (see *Scheme*). The kinetic equations thus obtained fit the peaking rate curves well throughout the range of unsaturated component concentrations in the binary systems. Our mathematical simulation was based on experimental data obtained for γ-radiation-induced addition reactions for which the initiation rate V_1 is known.

The analysis of stable liquid-phase products was carried out by the gas chromatographic method.
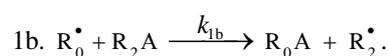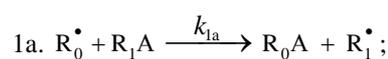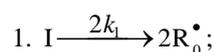
II. ADDITION TO THE C=C BOND OF ALKENES AND THEIR DERIVATIVES

When reacting with alkenes not inclined to free-radical polymerization, the free radicals originating from inefficient saturated telogens, such as alcohols [14] and amines [15], usually add to the least substituted carbon atom at the double bond, primarily yielding a free 1:1 adduct radical. This radical accumulates an energy of 90–130 kJ mol^{-1}, which is released upon the transformation of the C=C bond to an ordinary bond (according to the data reported for the addition of nonbranched C$_1$–C$_4$ alkyl radicals to propene and of similar C$_1$ and C$_2$ radicals to 1-butene in the gas phase under standard conditions [1–4]). Such adduct radicals, which do not decompose readily for structural reasons, can abstract the most labile atom from a neighbor molecule of the saturated or unsaturated component of the binary reaction system, thus turning into a 1:1 adduct molecule. The consecutive and parallel reactions involved in this free-radical nonbranched-chain addition process are presented below (*Scheme*). In the case of comparable component concentrations with a nonoverwhelming excess of the saturated component, extra reaction (1b) ($k_{1b} \neq 0$) is included in the initiation stage [8, 9]. In the case of an overwhelming excess of the saturated component reaction (1b) is ignored ($k_{1b} = 0$) [10, 11].
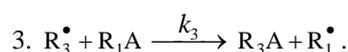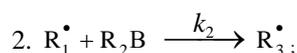
A. *Comparable Component Concentrations*

Scheme

Chain initiation

1. $I \xrightarrow{2k_1} 2R_0^\bullet$;

1a. $R_0^\bullet + R_1A \xrightarrow{k_{1a}} R_0A + R_1^\bullet$;

1b. $R_0^\bullet + R_2A \xrightarrow{k_{1b}} R_0A + R_2^\bullet$.

Chain propagation

2. $R_1^\bullet + R_2B \xrightarrow{k_2} R_3^\bullet$;

3. $R_3^\bullet + R_1A \xrightarrow{k_3} R_3A + R_1^\bullet$.

Inhibition

4. $R_3^{\bullet} + R_2 B \xrightarrow{k_4} R_3 B + R_2^{\bullet}$.

Chain termination

5. $2R_1^{\bullet} \xrightarrow{2k_5} \text{Prod}$;

6. $R_1^{\bullet} + R_2^{\bullet} \xrightarrow{k_6} \text{Prod}$;
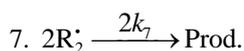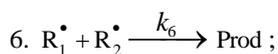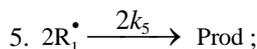
7. $2R_2^{\bullet} \xrightarrow{2k_7} \text{Prod}$.
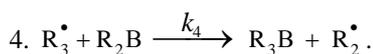
In this scheme, I is an initiator (e.g., a peroxide [5]); $R_0^{\bullet}$ is a reactive (initiating) radical; A and B are hydrogen or halogen atoms [2, 5, 14–21]; $R_1^{\bullet}$ is $^{\bullet}PCl_2$ [16], $^{\bullet}CCl_3$ [27], alkyl [2, 5], 1-hydroxyalkyl [5, 6, 14, 19–21], or a similar functionalized reactive addend radical [5]; $R_2^{\bullet}$ is an alkenyl radical (allyl or higher) [2, 5, 14–19], 1-hydroxyalkenyl [5, 14, 15, 20, 21], or a similar functionalized low-reactive radical (inhibitor) [5, 15]; $R_3^{\bullet}$ is a saturated reactive 1:1 adduct radical; R_0A, R_0B, and R_1A are saturated molecules; R_2B is an unsaturated molecule (alkene or its derivative); R_3A and R_3B are 1:1 adduct molecules; Prod designates the molecular products resulting from the dimerization or disproportionation of free radicals. The chain evolution (propagation and inhibition) stage of *Scheme* include consecutive reactions 2 and 3, parallel (competing) reaction pairs 3 and 4, and consecutive-parallel reaction pair 2–4.

The initiation reaction 1 is either the decomposition of a chemical initiator [5, 14, 15] or a reaction induced by light [5, 17, 18] or ionizing radiation [16–20]. The overall rate of chain initiation (reactions 1, 1a, and 1b) is determined by the rate of the rate-limiting step ($k_{1b} > k_{1a}$). The reaction between the free radical $R_2^{\bullet}$, which results from reactions 1b and 4, and the saturated molecule R_1A is energetically unfavorable because it implies the formation of the free radical $R_1^{\bullet}$, which is less stable than the initial one. The addition reaction 2 may be accompanied by the abstraction reaction 2a.

$R_1^{\bullet} + R_2 B \xrightarrow{k_{2a}} R_1 B + R_2^{\bullet}$ which yields the product R_1B *via* a nonchain mechanism. Reaction 2a does not regenerate the addend radical $R_1^{\bullet}$ and is not necessary for a kinetic description of the process, because the rate ratio of reactions 2 and 2a, $V_2/V_{2a} = k_2/k_{2a}$, is independent of the concentration of the unsaturated component R_2B in the system. The inhibition of the nonbranched-chain addition process is due to reaction 4, in which the adduct radical $R_3^{\bullet}$ is spent in an inefficient way, since this reaction, unlike reaction 3, does not regenerate $R_1^{\bullet}$. The inhibiting effect is also due to the loss of chain carriers $R_1^{\bullet}$ through their collisions with low-reactive unsaturated radicals $R_2^{\bullet}$, but to a much lesser extent.

The rates of the formation (V, mol dm^{-3} s^{-1}) of the 1:1 adducts R_3A (*via* a chain mechanism) and R_3B (*via* a nonchain mechanism) in reactions 3 and 4 are given by the equations

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

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

where V_1 is the rate of the initiation reaction 1; $l = [R_1A]$ and $x = [R_2B]$ are the molar concentrations of the initial components, with $l > x$; k_2 is the rate constant of the addition of the $R_1^{\bullet}$ radical from the saturated component R_1A to the unsaturated molecule R_2B (reaction 2); and $\gamma = k_{1a}/k_{1b}$ and $\alpha = k_3/k_4$ are the rate constant ratios for competing (parallel) reactions (α is the first chain-transfer constant for the free-radical telomerization process [5]). The rate ratio for the competing reactions is $V_3/V_4 = \alpha l/x$, and the chain length is $\nu = V_3/V_1$.

Earlier mathematical simulation [8] demonstrated that replacing the adduct radical R_3 with the radical R_2 [5] in the reaction between identical radicals and in the reaction involving R_1 gives rise to a peak in the curve of the 1:1 adduct formation rate as a function of the concentration of the unsaturated component. Reaction 1b, which is in competition with reaction 1a, is responsible for the maximum in the curve described by Eq. (2), and reaction 4, which is in competition with reaction (3), is responsible for the maximum in the curve defined by Eq. (1).

The number of unknown kinetic parameters to be determined directly (k_2, α, and γ) can be reduced by introducing the condition $\gamma \cong \alpha$, which is suggested by the chemical analogy between the competing reactions pairs 1a–1b and 3–4. For example, the ratios of the rate constants of the reactions of $^{\bullet}OH$, $CH_3O^{\bullet}$, $^{\bullet}CH_3$, $NO_3^{\bullet}$, and $H_2PO_4^{\bullet}$ with methanol to the rate constants of the reactions of the same radicals with ethanol in aqueous solution at room temperature are 0.4–0.5 [22, 23]. For the same purpose, the rate constant of reaction 2 in the kinetic equation can be replaced with its analytical expression $k_2 = \alpha l_m \sqrt{2k_5 V_1} / x_m^2$, which is obtained by solving the quadratic equation following from the reaction rate extremum condition $\partial V_{3,4}(1:1\,\text{Adduct}) / \partial x = 0$, where $\partial V_{3,4}(1:1\,\text{Adduct}) = V_3 + V_4$. After these transformations, the overall formation rate equation for the 1:1 adducts R_3A and R_3B (which may be identical, as in the case of R_3H [5, 8, 9, 15–18]), appears as

$$V_{3,4}(1:1\,\text{Adduct}) = \frac{V_1 \alpha l k_2 x}{k_2 x^2 + (\alpha l + x)\sqrt{2k_5 V_1}} = \qquad (3)$$

$$= \frac{V_1 \alpha l x}{x^2 + (\alpha l + x) x_m^2 / \alpha l_m}, \quad (3a)$$

where l_m and x_m are the component concentrations l and x at the points of maximum of the function. Provided that V_1 is known, the only parameter in Eq. (3a) to be determined directly is α. If V_1 is known only for the saturated component R_1A, then, for the binary system containing comparable R_1A and R_2B concentrations, it is better to use the quantity λV_1, where $\lambda = l/(l + x)$ is the mole fraction of R_1A, in place of V_1 in Eqs. (3) and (3a).

The two variable concentrations in the kinetic equation (3) – l and x – can be reduced to one variable by replacing them with the corresponding mole fractions. Substituting the expression

$$k_2 = \left\{ \alpha \left[(1/\chi_m) - 1 \right]^2 - 1 \right\} \sqrt{2 k_5 V_1} \Big/ (l_m + x_m), \text{ derived}$$

from the rate extremum condition, into this transformed equation for the binary system containing comparable component concentrations, we obtain

$$V_{3,4} (\text{Adduct } 1:1) =$$

$$\frac{V_1 \alpha (1 - \chi) \chi}{\chi^2 + [\alpha(1 - \chi) + \chi] \Big/ \left\{ \alpha [(1/\chi_m) - 1]^2 - 1 \right\}}, \quad (3b)$$

where $1 - \chi = l/(l + x)$ and $\chi = x/(l + x)$ are the mole fractions of the components R_1A and R_2B ($0 < \chi < 1$), respectively, and χ_m is the χ value at the point of maximum.

The overall formation rate of the 1:1 adducts R_3A and R_3B is a sophisticated function of the formation and disappearance rates of the radicals $R_1^\bullet$ and $R_2^\bullet$: $V(R_3A, R_3B) = (V_{1a} + V_3 - V_5) - (V_{1b} + V_4 - V_7)$.

The application of the above rate equations to particular single nonbranched-chain additions is illustrated in Fig. 1. Curve *1* represents the results of simulation in terms of Eq. (3b) for the observed 1:1 adduct formation rate as a function of the mole fraction of the unsaturated component in the phosphorus trichloride–methylpropene[2] reaction system at 303 K [16]. In this simulation, the ^{60}Co γ-radiation dose rate was set at $P = 0.01$ Gy s^{-1} and the initiation yield was taken to be $G(^\bullet PCl_2) = 2.8$ particles per 100 eV (1.60×10^{-17} J) of the energy absorbed by the solution [16]. The product of reaction 3 is $Cl_2PCH_2C(Cl)(CH_3)CH_3$ (two isomers), $V_1 = 4.65 \times 10^{-9}$ mol dm^{-3} s^{-1} at $\chi = 0$, and $2k_5 = 3.2 \times 10^8$ dm^3 mol^{-1} s^{-1}. This leads to $\alpha = (2.5 \pm 0.4) \times 10^3$, and the rate constant of reaction 2 derived from this α value is $k_2 = (1.1 \pm 0.2) \times 10^4$ dm^3 mol^{-1} s^{-1}.
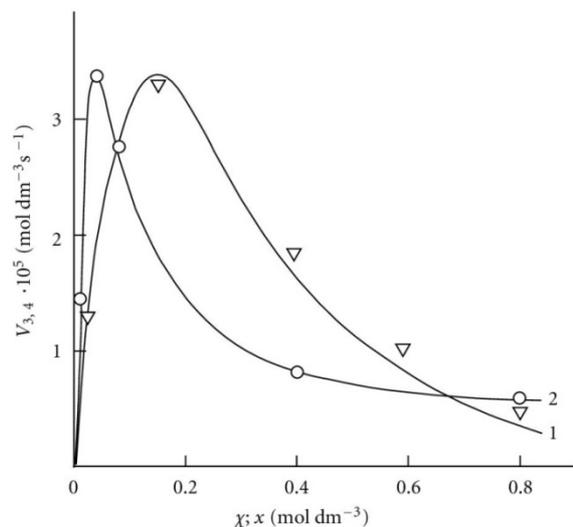

Figure 1. Reconstruction of the functional dependences (curves) of the product formation rates $V_{3,4}$ (*1*, $\triangledown$) on the mole fraction of the unsaturated component (χ) from empirical data (symbols) using Eq. (3b) (model optimization with respect to the parameter α) for the phosphorus trichloride–methylpropene reaction system at 303 K [16] (standard deviation of $S_Y = 2.58 \times 10^{-6}$) and (*2*, $\circ$) on the concentration of the unsaturated component (x) from empirical data (symbols) using Eq. (4a) (model optimization with respect to V_1, x_m, and α) for the 2-propanol–2-propen-1-ol system at 433 K [20] ($S_Y = 5.91 \times 10^{-7}$).

Note that, if the R_2–B bond dissociation energy for the unsaturated component of the binary system is approximately equal to or above, not below, the R_1–A bond dissociation energy for the saturated component, then the rate of reaction 4 relative to the rate of the parallel reaction 3 (chain propagation through the reactive free radical $R_1^\bullet$) will be sufficiently high for adequate description of R_3A and R_3B adduct formation in terms of Eqs. (1)–(3b) only at high temperatures [17]. In the phosphorus trichloride–propene system, the difference between the R_2–B (B = H) and R_1–A (A = Hal) bond dissociation energies in the gas phase under standard conditions [1] is as small as 5 kJ mol^{-1}, while in the tetrachloromethane–methylpropene (or cyclohexene) and bromoethane–2-methyl-2-butene systems, this difference is 20.9 (37.7) and ~24 kJ mol^{-1}, respectively.

B. Excess of the Saturated Component

If the concentration of the saturated component exceeds the concentration of the unsaturated component in the binary system, reaction 1b can be neglected. If this is the case ($k_{1b} = 0$), then, in the numerators of the rate equations for reactions 3 and 4 (Eqs. (1) and (2)), $\gamma l/(\gamma l + x) = 1$ and the overall rate equation for the formation of the 1:1 adducts R_3A and R_3B will appear as

$$V_{3,4} (\text{1:1 Adduct}) = \frac{V_1 (\alpha l + x) k_2 x}{k_2 x^2 + (\alpha l + x) \sqrt{2 k_5 V_1}} = \quad (4)$$

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[2] In an earlier work [10], the methylpropene concentration in this system was overvalued by a factor of 1.7 when it was derived from the mole fractions given in [19].

$$= \frac{V_1 x}{\dfrac{x^2}{\alpha l + x} + \left(\dfrac{\sqrt{\alpha l_m}}{x_m} + \dfrac{1}{\sqrt{\alpha l_m}}\right)^{-2}}, \quad (4a)$$

where the parameters are designated in the same way as in Eqs. (1)–(3a), $l \gg x$, and $k_2 = \left[\left(\sqrt{\alpha l_m}/x_m\right) + \left(1/\sqrt{\alpha l_m}\right)\right]^2 \sqrt{2k_5 V_1}$ is determined from the condition $\partial V_{3,\,4}(\text{1:1 Adduct})\,/\,\partial x = 0$.

The rate equations for the chain termination steps (reactions 5–7 in the *Scheme*; $k_{1b} = 0$) are identical to the equations reported for these steps in [24] if $\beta = 0$ in those equations.

Note that, if it is necessary to supplement *Scheme* for $k_{1b} = 0$ with the formation of R_1B *via* the possible nonchain reaction 2a (which is considered in the Section 2.1), the parameter k_{2a} should be included in the denominator of Eq. (4) to obtain $k_2 x^2 + (\alpha l + x)(k_{2a}x + \sqrt{2k_5 V_1})$.

The analytical expression for k_2 in the case of $k_{2a} \neq 0$ is identical to the expression for k_2 for Eq. (4). The equation for the rate $V_{2a}(R_1B)$ can be derived by replacing k_2 with k_{2a} in the numerator of Eq. (4) containing k_{2a} in its denominator.

Curve *2* in Fig. 1 illustrates the good fit between Eq. (4a) and the observed 1:1 adduct formation rate as a function of the concentration of the unsaturated component in the reaction system 2-propanol–2-propen-1-ol at 433 K [8, 9]. In this description, we used a ^{60}Co γ-radiation dose rate of $P = 4.47$ Gy s^{-1} [20]. The product of reactions 3 and 4 is $CH_3(CH_3)C(OH)CH_2CH_2CH_2OH$, and $2k_5 = 1.0 \times 10^{10}$ dm^3 mol^{-1} s^{-1}. The following parameters were obtained: $V_1 = (3.18 \pm 0.4) \times 10^6$ mol dm^{-3} s^{-1}, $x_m = (3.9 \pm 0.5) \times 10^{-2}$ mol dm^{-3}, and $\alpha = (6.8 \pm 0.8) \times 10^{-2}$. The rate constant of reaction 2 derived from this α is $k_2 = (1.0 \pm 0.14) \times 10^5$ dm^3 mol^{-1} s^{-1}.

III. CONCLUSIONS

In summary, the material on the kinetics of nonbranched-chain addition of free saturated radicals to double bonds of molecules of alkene and its derivative makes it possible to describe, using rate equations (3) and (4) obtained by quasi-steady-state treatment, experimental dependences with a maximum of the formation rates of molecular 1:1 adducts on the concentration of an unsaturated compound over the entire region of its change in binary reaction systems consisting of saturated and unsaturated components (Fig. 1).

The proposed addition mechanism involves the reaction of a free 1:1 adduct radical with an unsaturated molecule yielding a low-reactive free radical (the reaction 4 competing with the chain propagation reactions in *Scheme*). In such reaction systems, the unsaturated compound is both a reactant and an autoinhibitor,

specifically, a source of low-reactive free radicals shortening kinetic chains.

The optimum concentration x_m of unsaturated component in the binary system at which the process rate is maximal can be derived with the help of obtained kinetic equations (3a) and (4a) or from the corresponding analytical expressions for k_2 if other parameters are known. This opens a way to intensification of some technological processes that are based on the addition of free radicals to the double bonds of unsaturated molecules and occur *via* a nonbranched-chain mechanism through the formation of 1:1 adducts.

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