Simulation of Nonbranched Chain Processes for Producing 1,2-Alkanediols in Alcohol–Formaldehyde Systems

M. M. Silaev

Moscow State University, Moscow, 119992 Russia
e-mail: mmsilaev@rc.chem.msu.ru
Received November 16, 2006

Abstract—A mechanism of the initiated nonbranched chain process of forming 1,2-alkanediols and carbonyl compounds in alcohol–formaldehyde systems is developed. The quasi-steady-state treatment is used to obtain kinetic equations that can describe the nonmonotonic (with a maximum) dependences of the formation rates of the products on the concentration of free (desolvated) dissolved formaldehyde.

DOI: 10.1134/S0040579507040045

1-Hydroxyalkyl radicals are added to the carbon atom belonging to the double bond of the carbonyl group in the free (desolvated, monomer) formaldehyde dissolved in a saturated alcohol [1–6]. The concentration of free formaldehyde in the solution at room temperature is equal to several percent fractions of its total concentration, which also includes the formaldehyde chemically bound to the solvent [7]. The concentration of free formaldehyde exponentially increases with increasing temperature [10].[1] The energy released as a result of this addition, when the C = O double bond is converted into a simple one, is 30 to 60 kJ/mol according to the data on the addition of alkyl C_1–C_4 radicals in the gas phase under standard conditions [11–14]. The resulting free 1:1 adduct radicals can not only abstract hydrogen atoms from the closest molecules of the solvent or desolvated formaldehyde but also be subject due to its structure to decomposition by the monomolecular mechanism, which includes isomerization [15, 16].

The present paper presents the complete scheme of reactions necessary for the mathematical simulation of the initiated hydroxymethylation of saturated aliphatic alcohols. This scheme includes a reaction of abstracting a hydrogen atom from the molecule of free formaldehyde by an adduct hydroxyalkoxyl radical, which is competing to the reactions of chaining through active free radicals. This reaction results in a low-reactive free formyl radical, which inhibits the nonbranched chain addition.

---

[1] The concentration of alcohol in alcohol–formaldehyde solutions at any temperature can be estimated by the method [8, 9]. The data necessary for estimating the concentration of free formaldehyde using its total concentration in the solution are reported by Silaev et al. [9, 10].
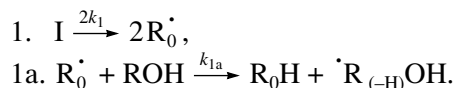
ADDITION OF FREE 1-HYDROXYALKYL RADICALS WITH TWO AND MORE CARBON ATOMS

Free 1-hydroxyalkyl radicals, which are formed as a result of abstracting a hydrogen atom from the carbon atom bounded to the hydroxide group in molecules of saturated aliphatic alcohols (except for methanol) under the action of chemical initiators [1, 2], light [17], or ionizing radiation [3–6], are added through the double bond of the free formaldehyde dissolved in the alcohol, forming 1,2-alkanediols [1, 6, 15, 16], carbonyl compounds, and methanol [5, 15] by the chaining mechanism. In this case, the yields of the latter two products in the temperature range of 303 to 448 K are one order of magnitude lower. In these processes, the determining role in the reactivity of the alcohols can be played by the desolvation of formaldehyde in alcohol–formaldehyde solutions, which depends both on the temperature and the polarity of the solvent [9, 10]. For the γ-radiolysis of 1(or 2)-propanol–formaldehyde systems at constant temperature, the curves of the radiation-chemical yields of 1,2-alkanediols and carbonyl compounds versus the formaldehyde concentration have a maximum and are symbatic [3, 4, 15]. For a constant total concentration of formaldehyde of 1 mol/dm^{-3}, the curves of 1,2-alkanediol yields versus the temperature for the range of 303 to 473 K have a maximum whereas the yields of carbonyl compounds and methanol are monotonically increasing [5] (along with the concentration of free formaldehyde [10]). In addition to the above products, the nonchained mechanism in the γ-radiolysis of the solutions of formaldehyde in ethanol, 1- and 2-propanol results in low radiation-chemical yields of ethanediol, carbon oxide, and hydrogen, which, however, exceed the yields of analogous products in the γ-radiolysis of individual alcohols [5, 15, 16]. The avail-
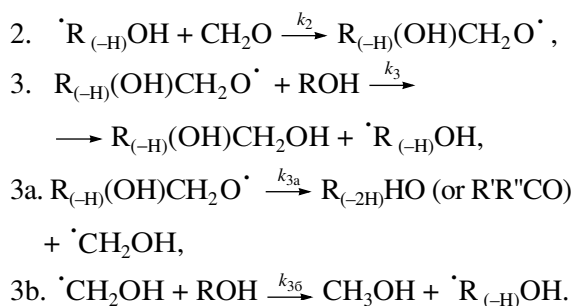
able experimental data can be described using the following scheme of reactions:
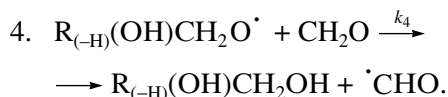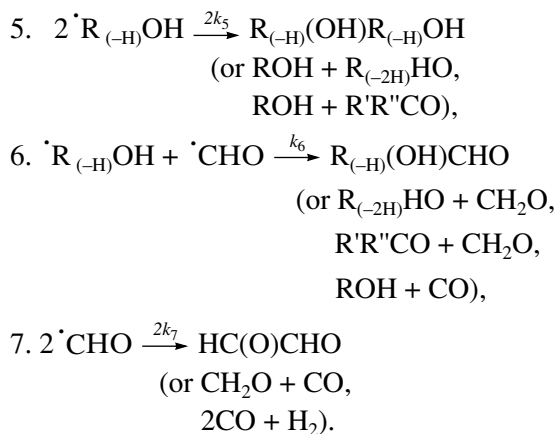
Scheme

Chain initiation:

1. $I \xrightarrow{2k_1} 2R_0^\bullet$,
1a. $R_0^\bullet + ROH \xrightarrow{k_{1a}} R_0H + {}^\bullet R_{(-H)}OH$.

Chain propagation:

2. ${}^\bullet R_{(-H)}OH + CH_2O \xrightarrow{k_2} R_{(-H)}(OH)CH_2O^\bullet$,

3. $R_{(-H)}(OH)CH_2O^\bullet + ROH \xrightarrow{k_3}$

$\longrightarrow R_{(-H)}(OH)CH_2OH + {}^\bullet R_{(-H)}OH$,

3a. $R_{(-H)}(OH)CH_2O^\bullet \xrightarrow{k_{3a}} R_{(-2H)}HO$ (or $R'R''CO$)

$+ {}^\bullet CH_2OH$,

3b. ${}^\bullet CH_2OH + ROH \xrightarrow{k_{36}} CH_3OH + {}^\bullet R_{(-H)}OH$.

Inhibition:

4. $R_{(-H)}(OH)CH_2O^\bullet + CH_2O \xrightarrow{k_4}$

$\longrightarrow R_{(-H)}(OH)CH_2OH + {}^\bullet CHO$.

Chain termination;

5. $2{}^\bullet R_{(-H)}OH \xrightarrow{2k_5} R_{(-H)}(OH)R_{(-H)}OH$

$(or\ ROH + R_{(-2H)}HO,$

$ROH + R'R''CO),$

6. ${}^\bullet R_{(-H)}OH + {}^\bullet CHO \xrightarrow{k_6} R_{(-H)}(OH)CHO$

$(or\ R_{(-2H)}HO + CH_2O,$

$R'R''CO + CH_2O,$

$ROH + CO),$

7. $2{}^\bullet CHO \xrightarrow{2k_7} HC(O)CHO$

$(or\ CH_2O + CO,$

$2CO + H_2).$

In these reactions, I is the initiator, such as peroxide [1, 2]; $R_0^\bullet$, some reactive radical (initiator radical); R, the alkyl; ROH, the saturated aliphatic alcohol, beginning with ethanol, primary or secondary; CH_2O, the unsaturated molecule: free formaldehyde; ${}^\bullet R_{(-H)}OH$, the reactive 1-hydroxyalkyl radical, beginning with 1-hydroxyethyl (addend radical); $R_{(-H)}(OH)CH_2O^\bullet$, the reactive hydroxyalkoxyl radical (adduct radical); ${}^\bullet CHO$, the low-reactive formyl radical (inhibitor radical); R_0H, the molecular product; $R_{(-H)}(OH)CH_2OH$, 1,2-alkanediol; $R_{(-2H)}HO$, the aldehyde in the case of a primary alcohol, or $R'R''CO$, the ketone in the case of a

secondary alcohol; $R_{(-H)}(OH)R_{(-H)}OH$, the vicinal alkanediol; $R_{(-H)}(OH)CHO$, the hydroxyaldehyde. At the stages of chain initiation and evolution, the scheme includes consecutive reactions 1, 1a; 2; 3; 3a, 3b; parallel (competing) reactions 3, 3a; 3, 4; 3a, 4; and consecutive–parallel reactions 2, 4.

The scheme does not include the possible abstraction reaction competing with addition reaction 2:

2a. ${}^\bullet R_{(-H)}OH + CH_2O \xrightarrow{k_{2a}} ROH + {}^\bullet CHO$,
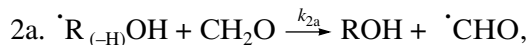
because the latter does not result in the regeneration of the ${}^\bullet R_{(-H)}OH$ addend radical. This reaction is not necessary for the kinetic description of the process because the ratio of rates $V_2/V_{2a} = k_2/k_{2a}$ for these reactions is independent of the concentration of the unsaturated component CH_2O in the system. In addition, the reaction of adding free adduct radicals to formaldehyde at higher temperatures is unlikely because it is accompanied by the formation of an ether bond. The reaction of adding hydroxymethyl radicals to formaldehyde, which is competing with reaction 3b, is not included as well because there is no chain formation of ethanediol in the range of temperatures of 303 to 448 K [5]. At the same time, its small amounts can be formed due to the dimerization of a small fraction of hydroxymethyl radicals, but this should not have some noticeable effect on the kinetic behavior of the process as a whole. The reaction of adding free formyl radicals to formaldehyde cannot be effective because of the absence of the chain formation of glycol aldehyde in the systems under study [5].

The mechanism of reaction 3a of decomposing a free adduct radical, which includes the formation of an internal H···O bond and isomerization, can be represented by the following scheme [15, 16]:
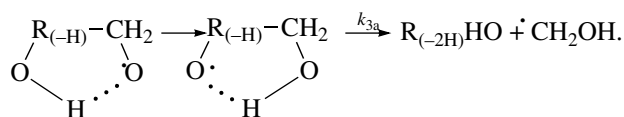
The probability of the occurrence of reaction 3a should increase with increasing temperature. This is supported by the experimental data discussed above [15, 16]. The reaction 3a of decomposing the $R_{(-H)}(OH)CH_2O^\bullet$ hydroxyalkoxyl radical appears to be endothermic. The endothermic nature of reaction 3a is indirectly indicated by the fact that the decomposition of simple alkoxyl C_2–C_4 radicals $RO^\bullet$ in the gas phase is accompanied by the absorption of heat: $\Delta H^\circ_{298} = 30$ to 90 kJ/mol [12–14]. The reaction 3b, which follows reaction 3a, is exothermic, and its heat effect for C_2–C_3 alcohols in the gas phase is $\Delta H^\circ_{298} = -40$ to -60 kJ/mol [12–14]. As it follows from the given scheme of the process, reaction 3a together with reaction 3b accompanied by the formation and consumption of a highly reactive free hydroxymethyl radical (their rates should be equal under steady-state conditions) can be repre-

sented as one common bimolecular reaction 3a,b, which proceeds in the "cell" consisting of solvent molecules.

The free formyl radicals formed in reaction 4, which is competing with reactions 3 and 3a, are relatively low-reactive because the spin density can be partially delocalized from the carbon atom via the double bond toward the oxygen, which possesses a larger affinity for electron [11]. For example, in contrast to methyl and alkoxyl radicals, the formyl radicals are stabilized in glassy alcohols at 77 K [18]. The energy of stabilization a formyl radical in the gas phase under standard conditions is –24.3 kJ/mol [19]. In the gas phase, the dissociation energy for the C–H bond in formyl radicals is half that for acetyl radicals and about 5 times less than the dissociation energy for the C_α–H bond in C_1–C_3 saturated alcohols [11].

In contrast to reactions 3 and 3a,b, reaction 4 leads to an ineffective consumption of hydroxyalkoxyl adduct radicals, without regeneration of the initial 1-hydroxyalkyl addend radicals. Reaction 4 together with reaction 6 (mutual decay of free formyl and chain-carrier 1-hydroxyalkyl radicals) causes the inhibition of the nonbranched chain process. When the free radicals are disproportionated, the heat effects of reactions 5–7 for C_1–C_3 alcohols in the gas phase are varied in the following range: ΔH°_{298} = –135 to –385 kJ/mol [11–14].

The rates of the chain formation of 1,2-alkanediols in reaction 3 (and their unchained formation in reaction 4), carbonyl compounds in reaction 3a, and methanol in reaction 3b are determined by the equations [2]:

$$V_{3,4}(R_{(-H)}(OH)CH_2OH)$$

$$= \frac{V_1(\alpha l + x)k_2 x}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_5 V_1}}, \qquad (1)$$

$$V_{3a}(R_{(-2H)}HO) = V_{3b}(CH_3OH)$$

$$= \frac{V_1 \beta k_2 x}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_5 V_1}}, \qquad (2)$$

where V_1 is the initiation rate; l = [ROH] $\gg$ [CH$_2$O] = x. The estimated values of rate constants $2k_5$ are given by Silaev et al. [9, 22]. The extremum condition for the reaction rate function $\partial V_{3a}/\partial x = 0$ was used to find the following analytical expression: $k_2 = (\alpha l_m + \beta)\sqrt{2k_5 V_1}/x_m^2$.

---

[2] The rate equations were derived by quasi-steady-state treatment, which is most suitable for describing the processes including at least eight to ten reactions with four to six different free radicals and at most three to seven experimental points in their functional curves, using the condition for the first steps of the process that makes it possible to reduce the exponent of term $2k_5[^\bullet R_{(-H)}OH]^2$ to 1 in equation $d[R^\bullet]/dt = 0$ [15, 16]: $k_6 = \sqrt{2k_5 2k_7}$ [20] and $V_1 = V_5 + 2V_6 + V_7 = (\sqrt{2k_5}\ [^\bullet R_{(-H)}OH] + \sqrt{2k_7}\ [^\bullet CHO])^2$. The relations between the reaction rates and radiation-chemical yields for radiation-chemical processes are reported by Silaev [21].

Equations (1) and (2) taken on the condition that $k_2 x^2 \gg (\alpha l + x)\sqrt{2k_5 V_1}$ (the descending branch of the curve having a maximum) can be transformed to equations that can be used for a preliminary estimation of parameters α and β:

$$V_{3,4} = (V_1/\varphi)[(\alpha l/x) + 1], \qquad (1a)$$

$$V_{3a} = V_1 \beta / \varphi x, \qquad (2a)$$

where $\varphi = 2$ for the maximum (when $k_2 x^2 \cong (\alpha l + x)\sqrt{2k_5 V_1}$) and $\varphi = 1$ for the descending portion of the curve.

The overall rate of the process is a complex function of the rates of the reactions of forming and destroying $^\bullet R_{(-H)}OH$ and $^\bullet CHO$ free radicals:

$$V(R_{(-H)}(OH)CH_2OH, R_{(-2H)}HO, CH_3OH)$$

$$= V_{1a} + V_3 + V_{3b} - V_4 - V_5 + V_7.$$

The ratios of the rates of competing reactions are $V_3/V_4 = \alpha l/x$ and $V_{3a}/V_4 = \beta/x$, and the chain length is $\nu = (V_3 + V_{3a})/V_1$. The ratio of the rates of formation of 1,2-alkanediol and the carbonyl compound is a simple function of x:

$$V_{3,4}(R_{(-H)}(OH)CH_2OH)/V_{3a}(R_{(-2H)}HO)$$

$$= (k_4/k_{3a})x + (k_3/k_{3a})l.$$

The equations for the rates of chain-termination reactions 5–7 are identical to the corresponding equations given by Silaev [23].

The figure illustrates the use of Eqs. (1) and (2) for describing the experimental dependences of the formation rates of 1,2-butanediol (curve *1*) in reactions 3 and 4 and propionic aldehyde (curve *2*) in reaction 3a on the initial concentration of free formaldehyde in the 1-propanol–formaldehyde reacting system at a total formaldehyde concentration of 2.0 to 9.5 mol/dm^{-3} and temperature of 413 K [3, 15]. In this case, the dependence for the formation of propionic aldehyde was described using, as most reliable, the estimates of kinetic parameters that resulted from the description of a similar dependence for the formation of 1,2-butanediol, because the carbonyl compounds formed in alcohol–formaldehyde systems can react with the alcohol and this reaction considerably depends on the temperature and acidity of the medium [7]. The following values of the parameters were obtained: $\alpha = 0.36 \pm 0.07$, $\beta = 0.25 \pm 0.05$ mol/(dm^{-3}), $k_2 = (6.0 \pm 1.4) \times 10^3$ dm^3/(mol s). The mathematical modeling of the process was accomplished using a value of the dose rate of ^{137}Cs γ-radiation $P = 0.8$ Gy/s [3, 4] and a total initiation yield $G(CH_3CH_2{}^\bullet CHOH) = 9.0$ particles per 100 eV [15, 16] ($V_1 = 4.07 \times 10^{-7}$ mol/(dm^3 s), and $2k_5 = 4.7 \times 10^9$ dm^3 /(mol s)).

It should be noted in summary that, as compared with the yields of 1,2-propanediol in the γ-radiolysis of
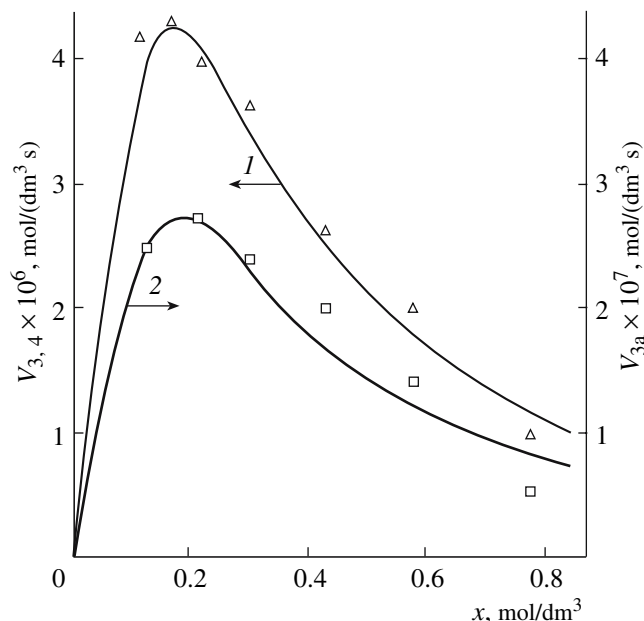
The reconstruction of the functional dependences of the rates of product formation $V_{3,4}$ (curve 1) and V_{3a} (curve 2) on the initial concentration x of free formaldehyde (optimization of the model by parameters α, β, and k_2) using empirical data (symbols) for the 1-propanol–formaldehyde system [3, 15]: curve 1, calculation by Eq. (1) with a standard deviation of function approximation $S_Y = 2.20 \times 10^{-7}$; curve 2, calculation by Eq. (2) with $S_Y = 2.38 \times 10^{-8}$.

the ethanol–formaldehyde system, the yields of 2,3-butanediol in the γ-radiolysis of the ethanol–acetaldehyde are one order of magnitude less [3]. Data [15, 16] can be used to show that the efficiency of accepting a 1-hydroxyethyl radical by the double bond of 2-propane-1-ol at a temperature of 433 K is 3.4 times higher than that for the double bond of formaldehyde [24].

ADDITION OF FREE HYDROXYMETHYL RADICALS

The addition of hydroxymethyl radicals to the carbon atom at the double bond of free-formaldehyde molecules in the solutions of formaldehyde in methanol, which is initiated by the free-radical mechanism, results in the chain formation of ethanediol. In this case, reaction 3a in the scheme will represent the reverse step of reaction 2; 1-hydroxyalkyl radicals $^\bullet R_{(-H)}OH$ become identical to hydroxymethyl radicals $^\bullet CH_2OH$, which annuls reaction 3b ($k_{3b} = 0$); reaction 5 will be characterized by the additional formation of ethanediol resulting from the dimerization of chain-carrier hydroxymethyl radicals (the reaction of their disproportionation practically can be ignored [25]).

The equation of rate $V_{3,4,5}$ for the formation of ethanediol by the chain mechanism in reaction 3 and by the unchained mechanism in reaction 4 and 5 in the methanol–formaldehyde system has a complicated form[3] as compared to Eq. (1) for the formation rate of other 1,2-alkanediols:

$$V_{3,4,5}(CH_2OH)_2 = V_1[f(\alpha l + x)k_2 x + V_1 2k_5(\alpha l + \beta + x)^2]/f^2, \qquad (3)$$

where $f = k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_5 V_1}$.

Equation (3) when $k_2 x^2 \ll (\alpha l + \beta + x)\sqrt{2k_5 V_1}$ (ascending branch of the curve having a maximum) and $\alpha l \gg \beta$ (practically without reaction 3a) is transformed to a simple directly-proportional dependence on the initial concentration x of free formaldehyde, which can be used to pre-estimate the parameter k_2:

$$V_{3,4,5} = (V_1/\varphi^2)[(\varphi k_2 x/\sqrt{2k_5 V_1}) + 1], \qquad (3a)$$

where $\varphi = 1$ for the ascending portion of the curve and $\varphi = 2$ for the maximum, when $k_2 x^2 \cong (\alpha l + \beta + x)\sqrt{2k_5 V_1}$.

If the small contribution of the formation of ethanediol by the dimerization mechanism in reaction 5 is ignored as compared to the contribution of its total formation in reactions 3 and 4, Eq. (3) will be identical to Eq. (1). After the numerator and denominator in the right side of Eq. (1) is divided by $k_{-2} \equiv k_{3a}$, one can replace k_2 with $K_2 = k_2/k_{-2}$, which is the equilibrium constant for reverse reaction 2. Ignoring the reverse step of reaction 2 ($k_{3a} = 0$, $\beta = 0$) can further simplify Eq. (1). In this case, the rate constant k_2 is effective.

NOTATION

k—reaction rate constant, $dm^3/(mol^{-1} s^{-1})$;

l—molar concentration of saturated alcohol ROH at a given total concentration of the formaldehyde dissolved in the alcohol, mol dm^{-3};

l_m, x_m—values of concentrations l and x of components at the point of maximum of the functionality;

x—initial molar concentration of free dissolved formaldehyde CH_2O, mol dm^{-3};

V—reaction rate, mol/(dm^3 s);

α, β—ratios of the rate constants of competing (parallel) reactions, k_3/k_4 and k_{3a}/k_4, respectively (dimension of the latter is mol dm^{-3}).

SUBSCRIPTS AND SUPERSCRIPTS

1, 2, …, 7—reaction number in the scheme of the process;

m—maximum value.

---

[3] In paper [15], this equation is reported without reaction 3a.

REFERENCES

1. Oyama, M., A Free-Radical Reaction of Primary and Secondary Alcohols with Formaldehyde, *J. Org. Chem.*, 1965, vol. 30, no. 7, p. 2429.

2. Nikishin, G.I., Lefor, D., and Vorob'ev, V.D., Free Radical Reaction of Primary Alcohols with Formaldehyde, *Izv. AN SSSR. Ser. Khim*, 1966, no. 7, p. 1271.

3. Shadyro, O.I., Radiation-chemical Conversions of Aldehydes in Various Systems, *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Minsk: Belorus. Gos. Univ., 1975.

4. Kalyazin, E.P., Petryaev, E.P., and Shadyro, O.I., Reaction between Oxyalkyl Radicals and Aldehydes, *Zh. Org. Khim.*, 1977, vol. 13, no. 2, p. 293.

5. Novoselov, A.I., Silaev, M.M., and Bugaenko, L.T., Effect of Temperature on the Yields of Final Products in the γ-Radiolysis of Formaldehyde Solutions in C_1–C_3 Alkanols, *Khim. Vys. Energ.*, 2004, vol. 38, no. 4, p. 270 [*High Energy Chem.* (Engl. Transl.), vol. 38, no. 4, p. 236].

6. Novoselov, A.I., Silaev, M.M., and Bugaenko, L.T., Dependence of 1,2-Propanediol Yield on Formaldehyde Concentration in γ-Radiolysis of Ethanol–Formaldehyde System at 373–473 K, *Khim. Vys. Energ.*, 2007, vol. 41, no. 1, p. 58 [*High Energy Chem.* (Engl. Transl.), vol. 41, no. 1, p. 53].

7. Ogorodnikov, S.K., *Formal'degid* (Formaldehyde), Leningrad: Khimiya, 1984.

8. Silaev, M.M., Estimation of the Solvent Concentration in Formaldehyde Solutions at Different Temperatures, *Zh. Fiz. Khim.*, 1993, vol. 67, no. 9, p. 1944.

9. Silaev, M.M., Applied Aspects of the γ-Radiolysis of C_1–C_4 Alcohols and Binary Mixtures on Their Basis, *Khim. Vys. Energ.*, 2002, vol. 36, no. 2, p. 97 [*High Energy Chem.* (Engl. Transl.), vol. 36, no. 2, p. 70].

10. Silaev, M.M., Rudnev, A.V., and Kalyazin, E.P., Formaldehyde. III. Concentration of Free Formaldehyde as a Function of Temperature, Polarity of Solvents, and Total Concentration of Formaldehyde in Solution, *Zh. Fiz. Khim.*, 1979, vol. 53, no. 7, p. 1647.

11. Gurvich, L.V., Karachevtsev, G.V., Kondrat'ev, V.N., Lebedev, Yu.A., Medvedev, V.A., Potapov, V.K., and Khodeev, Yu.S., *Energiya razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* (Chemical Bond Dissociation Energies. Ionization Potentials, and Electron Affinity), Kondrat'ev, V.N., Ed., Moscow: Nauka, 1974.

12. Benson, S.W., *Thermochemical Kinetics. Methods for the Estimation of Thermochemical Data and Rate Parameters*, New York: -Sidney-Toronto: Wiley & Sons, 1976.

13. Pedley, J.B., Naylor, R.D., and Kirby, S.P., *Thermochemical Data of Organic Compounds* London: Chapman & Hall, 1986, 2nd ed.

14. Orlov, Yu.D., Lebedev, Yu.A., and Saifullin, I.Sh., *Termokhimiya organicheskikh svobodnykh radikalov* (Thermochemistry of Free Organic Radicals), Kutepov, A.M., Ed., Moscow: Nauka, 2001.

15. Silaev, M.M. and Bugaenko, L.T., Mathematical Simulation of the Kinetics of Radiation Induced Hydroxyalkylation of Aliphatic Saturated Alcohols, *Radiat. Phys. Chem.*, 1992, vol. 40, no. 1, p. 1.

16. Silaev, M.M. and Bugaenko, L.T., The Kinetics of the Addition of α-Hydroxyalkyl Radicals to 2-propene-1-ol and Formaldehyde, *Kinet. Katal.*, 1994, vol. 35, no. 4, p. 509 [*Kinet. Catal.* (Engl. Transl.), vol. 35, no. 4, p. 463].

17. Urry, W.H., Stacey, F.W., Huyser, E.S., and Juveland, O.O., The Peroxide- and Light-Induced Additions of Alcohols To Olefins, *J. Am. Chem. Soc.*, 1954, vol. 76, no. 2, p. 450.

18. Sanderson, R.T., Radical Reorganization and Bond Energies in Organic Molecules, *J. Org. Chem.,* 1982, vol. 47, no. 20, p. 3835.

19. Pshezhetskii, S.Ya., Kotov, A.G., Milinchuk, V.K., Roginskii, V.A., and Tupikov, V.I., *EPR svobodnykh radikalov v radiatsionnoi khimii* (ESR of Free Radicals in Radiation Chemistry), Moscow: Khimiya, 1972.

20. Bateman, L., Olefin Oxidation, *Quart. Revs*, 1954, vol. 8, no. 2, p. 147.

21. Silaev, M.M., Simulation of the Nonbranched-Chain Addition of Saturated Free Radicals to Alkenes and Their Derivatives Yielding 1 : 1 Adducts, *Teor. Osn. Khim. Tekhnol.*, 2007, vol. 41, no. 3, p. 289 [*Theor. Found. Chem. Eng.* (Engl. Transl.), vol. 41, no. 3, p. 273].

22. Silaev, M.M., Bugaenko, L.T., and Kalyazin, E.P., On the Possibility of Adequately Estimating the Rate Constants for the Reaction of Hydroxyalkyl Radicals with Each Other Using the Self-Diffusion Coefficients or Viscosities of the Corresponding Alcohols, *Vestn. Mosk. Univ., Ser. 2, Khim*, 1986, vol. 27, no. 4, p. 386.

23. Silaev, M.M., The Competition Kinetics of Radical-Chain Addition, *Zh. Fiz. Khim.*, 1999, vol. 73, no. 7, p. 1180 [*Russ. J. Phys. Chem.* (Engl. Transl.), vol. 73, no. 7, p. 1050].

24. Silaev, M.M., Relative Reactivity of α-Hydroxyethyl Radicals for 2-Propene-1-ol and Formaldehyde Double-Bond Addition, *Vestn. Mosk. Un-Ta, Ser. 2, Khim*, 1993, vol. 34, no. 3, p. 311.

25. Seki, H., Nagai, R., and Imamura, M., γ-Radiolysis of a Binary Mixture of Methanol and Water. The Formation of Formaldehyde in the Radiolysis of Liquid Methanol, *Bull. Chem. Soc. Jpn.*, 1968, vol. 41, no. 12, p. 2877.