The Free-Radical Nonbranched-Chain Initiated Formation of Ethylene Glycol from Methanol–Formaldehyde Solutions

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Abstract: The mechanism and kinetics are developed for the free-radical nonbranched-chain initiated formation of ethylene glycol in methanol–formaldehyde solutions at formaldehyde concentrations of 0.1–3.1 mol dm^{-3} and temperatures of 373–473 K. The experimental concentrations of the free unsolvated form of formaldehyde are given at the different temperatures and total concentrations of formaldehyde in methanol. The experimental dependence of the radiation-chemical yields of ethylene glycol on formaldehyde concentration in γ-radiolysis of methanol–formaldehyde solutions at 373–473 K is shown. At a formaldehyde concentration of 1.4 mol dm^{-3} and T = 473 K, the radiation-chemical yield of ethylene glycol is 139 molecules per 100 eV. The effective activation energy of ethylene glycol formation is 25 ± 3 kJ mol^{-1}. The quasi-steady-state treatment of the reaction network suggested here led to a rate equation accounting for the non-monotonic dependence of the ethylene glycol formation rate on the concentration of the free (unsolvated) form of dissolved formaldehyde. It is demonstrated that the peak in this dependence is due to the competition between methanol and CH$_2$=O for reacting with adduct radical HOCH$_2$CH$_2$O$^{\cdot}$.

Keywords: Methanol, Formaldehyde, Formation, Ethylene Glycol, Radiation-Chemical Yield, Rate Equation.

I. INTRODUCTION

Ethylene glycol is widely used in the production of polyester fibers and films, antifreeze, hydraulic and quench liquids, alkyds, polyurethanes, etc. The primary commercial method of ethylene glycol synthesis is ethylene oxide hydration. The annual world ethylene glycol output is over 20 million tons.

These facts stimulate the development of new, energetically efficient ethylene glycol synthesis technologies. A possible one is a radiation-chemical synthesis using a dual-purpose heterogeneous nuclear reactor in which the graphite moderator is replaced with methanol–formaldehyde mixture and the heat carrier is steam flowing past fuel elements. A technological analysis of this system demonstrated that, at a reactor thermal power of 2.5 GW, it is possible to profitably manufacture 80 thousand tons of ethylene glycol per year along with producing 677 MW electric power.

Here, we report the experimental dependences of the radiation-chemical yield of ethylene glycol on the total formaldehyde concentration at different temperatures and present the reaction network deduced for the process examined. By applying quasi-steady-state treatment to this network, we obtain a rate equation for ethylene glycol formation.

II. EXPERIMENTAL

The experimental procedure used in this study, including the gas chromatographic analysis of stable products, was described in our earlier publication [1]. The concentration x of the free formaldehyde species in a methanol solution was determined by high-temperature UV spectrophotometry in the range 375–391 K at the total formaldehyde concentration c_0 (free and bound species including the concentration of polymer solvates) of 1.0–7.0 mol dm^{-3}. The ^{60}Co γ-radiation dose rate was 6.9 Gy s^{-1}, as determined with a ferrous sulfate dosimeter. The dose absorbed by the solution with the electron density of methanol taken into account was (1.25–6.28) × 10^4 Gy. The total relative error of the experiment was ≤10 %.

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 $2k_5[^{\cdot}\mathrm{CH_2OH}]^2$ to 1 in equation $d[^{\cdot}\mathrm{CH_2OH}]/dt = 0$: $k_6 = \sqrt{2k_5 2k_7}$ and $V_1 = V_5 + 2V_6 + V_7 = (2k_5[^{\cdot}\mathrm{CH_2OH}] + 2k_7[^{\cdot}\mathrm{CHO}])^2$ [2].

III. RESULTS AND DISCUSSION

The effect of temperature on the yields of the ultimate products of the γ-radiolysis of formaldehyde solutions in saturated aliphatic alcohols was considered elsewhere [1]. 1-Hydroxyalkyl radicals add to the carbon atom at the double bond of the carbonyl group of the free (unsolvated, monomeric) form of formaldehyde dissolved in the saturated alcohol [3]. At room temperature, the concentration of this form in the solution is a fraction of a per cent of the total

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formaldehyde concentration (which includes the formaldehyde chemically bonded with the solvent), and it increases exponentially as the temperature is raised [4]. The solvent concentration in formaldehyde solutions at a given temperature can be estimated by the method suggested by Silaev [5].

Figure **1** shows the Arrhenius plot of the ethylene glycol yield for the γ-radiolysis of 0.9 mol dm^{-3} solutions of formaldehyde in methanol [1]. As the temperature is elevated from 373 to 473 K, the free formaldehyde concentration calculated from earlier data [4] increases from 2.78×10^{-3} to 0.16 mol dm^{-3}. The effective activation energy of ethylene glycol formation is 25 ± 3 kJ mol^{-1}.
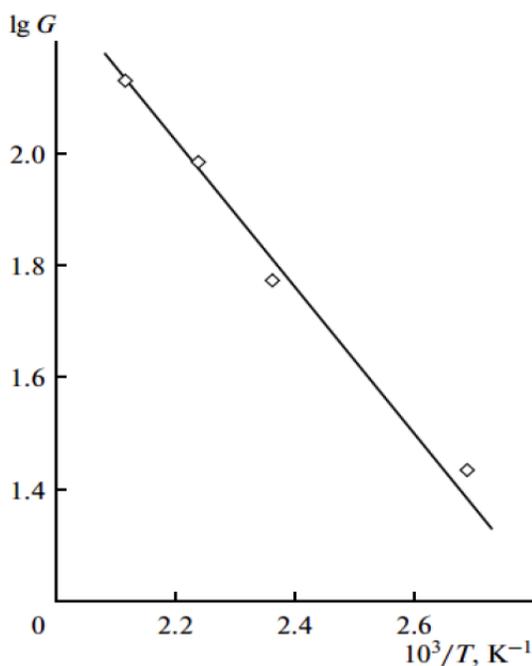

Figure 1: The logarithm of the ethylene glycol yield *G* (molecule/100 eV) versus inverse temperature for the γ-radiolysis of the methanol–formaldehyde (0.9 mol dm^{-3}) system [1].

Figure **2** plots the ethylene glycol yield as a function of the total concentration of formaldehyde (0.1, 0.3, 0.6, 0.9, 1.4, 2.2, and 3.1 mol dm^{-3}), including its free and alcohol-bound forms [3], in the methanol–formaldehyde system at 373, 423, 448, and 473 K [6]. The maximum product yield is 139 molecules per 100 eV (144 mol × 10^{-7} J) at a formaldehyde concentration of 1.4 mol dm^{-3} at 473 K.

There is no maximum in the product yield versus concentration curve at 373 K up to the highest formaldehyde concentration examined, 3.1 mol dm^{-3}. At higher temperatures, the curves have a maximum at

a formaldehyde concentration of about 1.4 mol dm^{-3}. The maximum in these curves arises from the competition between methanol and free formaldehyde (CH$_2$=O) for reacting with the adduct radical HOCH$_2$CH$_2$O$^{\bullet}$.
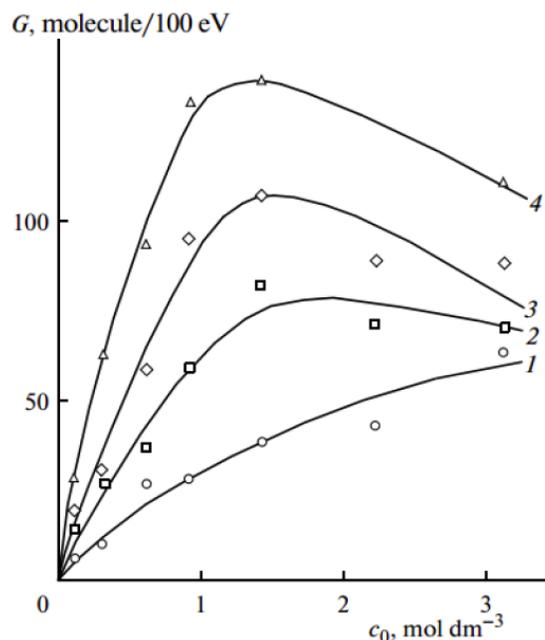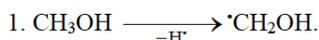

Figure 2: Ethylene glycol yield *G* as a function of the total formaldehyde concentration c_0 for the γ-radiolysis of the methanol–formaldehyde system at *T* = (*1*) 373, (*2*) 423, (*3*) 448, and (*4*) 473 K [6].

The main by-product of γ-radiolysis in the methanol–formaldehyde system is methylal, CH$_2$(OCH$_3$)$_2$, which results from the thermal acetalization of formaldehyde. The second most abundant by-product is methyl formate, CH$_3$OCHO, which also results from the reversible thermal conversion of formaldehyde [3, 7]. The concentrations of these products in the solution irradiated to a dose of 7.56×10^4 Gy at 473 K are, respectively, 0.56 and 0.08 mol dm^{-3}, which are 23.3 and 3.3 % of the total initial formaldehyde concentration in the system (2.4 mol dm^{-3}).
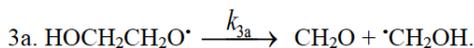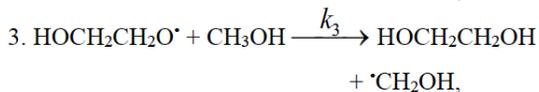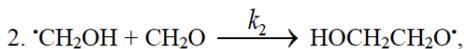
The kinetics of the initiated nonbranched-chain addition of 1-hydroxyalkyl radicals to free (unsolvated) formaldehyde CH$_2$=O in the γ-radiolysis of saturated aliphatic alcohol–formaldehyde systems, which yields vicinal glycols, carbonyl compounds, and methanol *via* a chain mechanism, was considered in earlier works [2, 8].

The data available on the methanol–formaldehyde system can be accounted for in terms of the following reaction network.
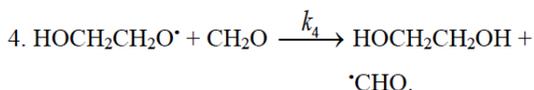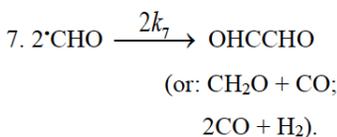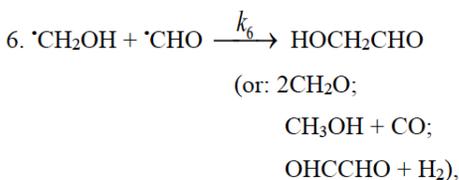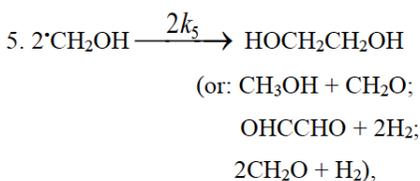
Chain initiation

1. $CH_3OH \xrightarrow[-H^\bullet]{} {}^\bullet CH_2OH.$

Chain propagation

2. ${}^\bullet CH_2OH + CH_2O \xrightarrow{k_2} HOCH_2CH_2O^\bullet,$

3. $HOCH_2CH_2O^\bullet + CH_3OH \xrightarrow{k_3} HOCH_2CH_2OH$
$+ {}^\bullet CH_2OH,$

3a. $HOCH_2CH_2O^\bullet \xrightarrow{k_{3a}} CH_2O + {}^\bullet CH_2OH.$

Inhibition

4. $HOCH_2CH_2O^\bullet + CH_2O \xrightarrow{k_4} HOCH_2CH_2OH +$
${}^\bullet CHO.$

Chain termination

5. $2{}^\bullet CH_2OH \xrightarrow{2k_5} HOCH_2CH_2OH$

(or: $CH_3OH + CH_2O$;

$OHCCHO + 2H_2$;

$2CH_2O + H_2$),

6. ${}^\bullet CH_2OH + {}^\bullet CHO \xrightarrow{k_6} HOCH_2CHO$

(or: $2CH_2O$;

$CH_3OH + CO$;

$OHCCHO + H_2$),

7. $2{}^\bullet CHO \xrightarrow{2k_7} OHCCHO$

(or: $CH_2O + CO$;

$2CO + H_2$).

In these reactions, ${}^\bullet CH_2OH$ is the reactive hydroxymethyl radical (addend), $HOCH_2CH_2O^\bullet$ is the reactive hydroxyethoxyl radical (adduct), ${}^\bullet CHO$ is the low-reactive formyl radical (inhibitor), $HOCH_2CH_2OH$ is ethylene glycol, $HOCH_2CHO$ is glycolaldehyde, and $OHCCHO$ glycol is glyoxal. Of the above molecular products, only ethylene glycol forms *via* a chain mechanism. Reaction 1 can be initiated by a peroxide [9], light [10], or γ-radiation [6].

The chain propagation and inhibition steps of reaction network include the pairs of consecutive reactions 2–3 and 2–3a; the pairs of parallel (competing) reactions 3–3a, 3–4, and 3a–4; and consecutive–parallel reactions 2 and 4. Reaction 3a is the reverse of reaction 2.

Reaction 5 yields an additional amount of ethylene glycol through the dimerization of the hydroxymethyl chain carrier radical. The disproportionation of this radical can be neglected [11].

The possible abstraction reaction

2a. ${}^\bullet CH_2OH + CH_2O \xrightarrow{k_{2a}} CH_3OH + {}^\bullet CHO,$
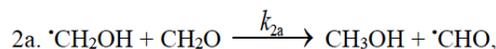
which is parallel to addition reaction 2, is not included in the reaction network for the reason that it does not regenerate the addend radical ${}^\bullet CH_2OH$. Besides, it is inessential for the kinetic description of the process because the rate ratio of these reactions, $V_2/V_{2a} = k_2/k_{2a}$, is independent of the concentration of the unsaturated component ($CH_2=O$) in the system. The addition of the adduct radical $HOCH_2CH_2O^\bullet$ to formaldehyde at elevated temperatures seems unlikely because it would yield an ether linkage.

The hydroxyethoxyl adduct radical $HOCH_2CH_2O^\bullet$ resulting from reaction 2 must possess an increased energy due to the energy released upon the conversion of the double bond C=O into an ordinary bond (30–60 kJ mol^{-1} for the addition of C_1–C_4 alkyl radicals to formaldehyde in the gas phase under standard conditions [12, 13]). Therefore, this radical is able both to abstract a hydrogen atom from the nearest methanol and formaldehyde molecules *via* reactions 3 and 4, respectively, and to decompose *via* a monomolecular mechanism including isomerization [2, 8] (reaction 3a) just on the spot, with- out diffusing in the solution and, accordingly, without participating in radical-radical termination reactions 5–7. A specific feature of the ethylene glycol buildup kinetics is that the decomposition reaction 3a of the adduct radical (whose probability increases with increasing temperature [8]) in the methanol–formaldehyde system is the reverse of the formation reaction 2 of this adduct radical.

The formyl radical ${}^\bullet CHO$ resulting from reaction 4, which is in competition with reactions 3 and 3a, is comparatively low-reactive because of the possibility of the partial delocalization of its spin density from the carbon atom *via* the double bond to oxygen, an element with a higher electron affinity [14]. For example, unlike the methyl and alkoxyl π-radicals, the formyl σ-radical can be stabilized in glassy alcohols at 77 K [15]. The stabilization energy of the formyl radical in the standard state in the gas phase is –24.3 kJ mol^{-1} [16]. In the gas phase, the C–H bond dissociation energy for the formyl radical is half the same energy for the acetyl radical and is almost 5 times lower than the $C\alpha$–H bond dissociation energy for the saturated C_1–C_3 alcohols [14]. As distinct from reactions 3 and 3a, reaction 4 wastes $HOCH_2CH_2O^\bullet$ adduct radicals without regenerating the chain-carrier addend radical

$^{\bullet}CH_2OH$, causing the termination of the kinetic chain through the formation of the low-reactive radical $^{\bullet}CHO$. Along with the $^{\bullet}CH_2OH + {}^{\bullet}CHO$ combination reaction 6, reaction 4 inhibits the nonbranched-chain process.

The following rate equation was set up by quasi-steady-state treatment for ethylene glycol formation *via* the chain mechanism (reaction 3) and the nonchain mechanism (reactions 4 and 5) [8]:

$$V_{3,4,5}(CH_2OH)_2 = V_1[f(\alpha l + x)k_2 x + V_1 2k_5(\alpha l + \beta + x)^2]f^{-2}, \quad (1)$$

where $f = k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_5 V_1}$; V_1 is the initiation rate, mol dm^{-3} s^{-1}; l – concentration (mol dm^{-3}) of methanol at a given concentration of formaldehyde dissolved in it, x – concentration (mol dm^{-3}) of free (unsolvated) formaldehyde, at that l = [CH$_3$OH] >> [CH$_2$=O] = x; $\alpha = k_3/k_4$ and $\beta = k_{3a}/k_4$ – ratios of the rate constants (dm^3 mol^{-1} s^{-1}) of the competing (parallel) reactions, the latter in units of mol dm^{-3}.

The experimental concentrations x of free (unsolvated) formaldehyde at different temperatures and total formaldehyde concentrations c_0, measured at room temperature, in methanol are given in the Table **1**. The free formaldehyde concentration x increases with the temperature according to an exponential law [4] and decreases with the solvent permittivity at a constant temperature [17].

The following empirical equation relating the concentration x (mol dm^{-3}) of free formaldehyde to temperature T (K) and the total concentration c_0 in the solution (measured at room temperature), was developed by the treatment of 101 data points [4]:

$$\lg x = -a\,(10^3/T) + b + h \lg c_0, \quad (2)$$

where the coefficients a and b were calculated as the parameters of a straight-line equation by the least-squares technique from the dependence of lg x on $1/T$ at c_0 = 1.0 mol dm^{-3} for various solvents, and the coefficient h was obtained as the average value of the slopes of lg x as linear functions of lg c_0 at various series of fixed temperatures. For methanol–formaldehyde solutions, the coefficients a = 3.11, b = 5.58, and h = 0.22 c_0 /lg c_0, the calculated concentrations x_{calc} of free formaldehyde are given in the Table **1**.

Note that Eq. (1) presented in a previous work [2] does not take into account reaction 3a. The rate ratios of the competing reactions are $V_3/V_4 = \alpha l/x$ and $V_{3a}/V_4 = \beta/x$, and the chain length is $v = (V_3 + V_{3a})/V_1$.

Table 1: Experimental x and calculated x_{calc} concentrations (mol dm^{-3}) of free (unsolvated) formaldehyde at different temperatures T (K) and total formaldehyde concentrations c_0 (mol dm^{-3}), measured at room temperature, in methanol [4]

c_0	T	$10^2 x$	$10^2 x_{calc}$
1.0	375	0.33	0.32
1.0	395	1.00	0.84
1.0	423	2.90	2.80
2.5	373	0.60	0.62
2.5	385	1.15	1.13
2.5	398	1.80	2.07
5.4	351	0.78	0.81
5.4	383	3.70	4.45
5.4	398	6.80	8.99
7.0	365	4.70	3.98
7.0	383	12.50	10.0
7.0	391	16.00	14.7

Equation (1) can be put into a simpler form [8] by ignoring the ethylene glycol yield from the dimerization reaction 5, which is insignificant as compared to the total ethylene glycol yield from reactions 3 and 4:

$$V_{3,\,4}(CH_2OH)_2 = \frac{V_1(\alpha l + x)k_2 x}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_5 V_1}}. \quad (3)$$

Dividing the numerator and denominator of Eq. (3) by $k_{-2} \equiv k_{3a}$ makes it possible to replace k_2 with $K_2 = k_2/k_{-2}$, the equilibrium constant of reversible reaction 2. Leaving aside the reverse of reaction 2 reaction 3a (k_{3a} = 0, β = 0) will further simplify Eq. (3). In this case, the rate constant k_2 will be an effective quantity.

Equation (1) 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 concentration x of free formaldehyde, which can be used to pre-estimate the parameter k_2:

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

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

Examples of fitting the experimental dependences of the vicinal glycol formation rate V (or radiation-chemical yield G) on the free formaldehyde concentration x in alcohol–formaldehyde systems to Eq. (2) are presented in earlier publications [2, 8].

The relationships between the reaction rates V and the radiation-chemical yields G are $V = GP$ and $V_1 = \varepsilon_1 G(\dot{C}H_2OH)P$, where P is the ionizing radiation dose rate, ε_1 is the electron fraction of methanol in the reaction system [18], and $G(\dot{C}H_2OH)$ is the primary yield of the hydroxymethyl chain-carrier radical – initiation yield.

IV. CONCLUSION

The mechanism and kinetics are developed for the initiated nonbranched-chain formation of ethylene glycol in methanol–formaldehyde solutions. The quasi-steady-state treatment of the reaction network suggested here yielded a rate equation describing the non-monotonic (peaking) dependence of the ethylene glycol formation rate on the concentration of the free (unsolvated) form of dissolved formaldehyde.

REFERENCES

[1] Novoselov AI, Silaev MM, Bugaenko LT. 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; 38(4): 270 [High Energy Chem (Engl Transl), 38(4): 236].
https://doi.org/10.1023/B:HIEC.0000035410.87205.09

[2] Silaev MM, Bugaenko LT. Mathematical Simulation of the Kinetics of Radiation Induced Hydroxyalkylation of Aliphatic Saturated Alcohols. Radiat Phys Chem 1992; 40(1): 1.
https://doi.org/10.1016/1359-0197(92)90131-X

[3] Ogorodnikov SK. Formal'degid (Formaldehyde), Leningrad: Khimiya 1984.

[4] Silaev MM, Rudnev AV, Kalyazin EP. Formaldehyde. III. The Concentration of Free Formaldehyde as a Function of Temperature, Solvent Polarity, and the Total Formaldehyde Concentration in the Solution. Zh Fiz Khim 1979; 53(7): 1647.

[5] Silaev MM. Estimating the Solvent Concentration in Formaldehyde Solutions at Various Temperatures. Zh Fiz Khim 1993; 67(9): 1944.

[6] Novoselov AI, Silaev MM, Bugaenko LT. Dependence of Ethanediol Yield on Formaldehyde Concentration in γ-Radiolysis of Methanol–Formaldehyde System at 373–473 K. Khim Vys Energ 2008; 42(1): 74-75 [High Energy Chem (Engl Transl), 42(1): 69-70].
https://doi.org/10.1134/S0018143908010141

[7] Yanovskaya LA, Yufit SS, Kucherov VF. Khimiya atsetalei (Chemistry of Acetals), Moscow: Nauka 1975.

[8] Silaev MM. Simulation of nonbranched chain processes for producing 1,2-alkanediols in alcohol-formaldehyde systems. Teor Osn Khim Tekhnol 2007; 41(4): 379 [Theor Found Chem Eng (Engl Transl), 41(4): 357].
https://doi.org/10.1134/S0040579507040045

[9] Oyama M. A Free-Radical Reaction of Primary and Secondary Alcohols with Formaldehyde. J Org Chem 1965; 30(7): 2429.
https://doi.org/10.1021/jo01018a079

[10] Dzhurinskaya MB, Rudnev AV, Kalyazin EP. High Temperature UV Photolysis of Formaldehyde in Liquid Methanol. Vestn Mosk Univ Ser 2: Khim 1984; 25(2): 173.

[11] Seki H, Nagai R, 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; 41(12): 2877.
https://doi.org/10.1246/bcsj.41.2877

[12] Orlov YuD, Lebedev YuA, Saifullin ISh. Termokhimiya organicheskikh svobodnykh radikalov (Thermochemistry of Organic Free Radicals), Kutepov, A.M., Ed., Moscow: Nauka 2001.

[13] Benson SW. Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters, New York: Wiley 1968.

[14] Gurvich LV, Karachevtsev GV, Kondrat'ev VN, Lebedev YuA. Medvedev VA, Potapov VK, Khodeev YuS. Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii I srodstvo k elektronu (Bond Dissociation Energies, Ionization Potentials, and Electron Affinity), Kondrat'ev, V.N., Ed., Moscow: Nauka 1974.

[15] Pshezhetskii SYa, Kotov AG, Milinchuk VK, Roginskii VA, Tupikov VI. EPR svobodnykh radikalov v radiatsionnoi khimii (ESR of Free Radicals in Radiation Chemistry), Moscow: Khimiya 1972; p. 212.

[16] Sanderson RT. Radical Reorganization and Bond Energies in Organic Molecules. J Org Chem 1982; 47(20): 3835.
https://doi.org/10.1021/jo00141a006

[17] Silaev MM. Applied Aspects of the γ-Radiolysis of C_1-C_4 Alcohols and Binary Mixtures on Their Basis. Khimiya Vysokikh Energii 2002; 36(2): 97-101 [High Energy Chem (Engl Transl), 36(2): pp. 70-74].

[18] Vereshchinskii IV, Pikaev AK. Vvedenie v radiatsionnuyu khimiyu (Introduction to Radiation Chemistry), Spitsyn, V.I., Ed., Moscow: Akad. Nauk SSSR 1963; p. 190.