

Kinetics of Initiated Ethanediol Formation from Methanol–Formaldehyde Solutions

Michael M. Silaev

Chemistry Faculty, Moscow State University, Moscow, 119991 Russia

Abstract — The mechanism and kinetics are developed for the initiated non branched-chain formation of ethanediol in methanol–formaldehyde solutions at formaldehyde concentrations of $0.1\text{--}3.1\text{ mol dm}^{-3}$ and temperatures of $373\text{--}473\text{ K}$. 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 ethanediol on formaldehyde concentration in γ -radiolysis of methanol–formaldehyde solutions at $373\text{--}473\text{ K}$ is shown. At a formaldehyde concentration of 1.4 mol dm^{-3} and $T = 473\text{ K}$, the radiation-chemical yield of ethanediol is 139 molecules per 100 eV. The effective activation energy of ethanediol formation is $25 \pm 3\text{ kJ mol}^{-1}$. The quasi-steady-state treatment of the reaction network suggested here led to a rate equation accounting for the non monotonic dependence of the ethanediol 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 $\text{CH}_2=\text{O}$ for reacting with the adduct radical $\text{HOCH}_2\text{CH}_2\text{O}^\bullet$.

Keywords — *Methanol, Formaldehyde, Formation, Ethanediol, Radiation-Chemical Yield, Rate Equation.*

I. INTRODUCTION

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

These facts stimulate development of new, energetically efficient ethanediol synthesis technologies. A possible one is radiation-chemical synthesis using a dual-purpose heterogeneous nuclear reactor in which the graphite moderator is replaced with a 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 ethanediol per year along with producing 677 MW electric powers.

Here, we report the experimental dependences of the radiation-chemical yield of ethanediol 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 ethanediol 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 $375\text{--}391\text{ K}$ at the total formaldehyde concentration c_0 (free and bound species including the concentration of polymer solvates) of $1.0\text{--}7.0\text{ mol dm}^{-3}$. 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 $(1.25\text{--}6.28) \times 10^4\text{ Gy}$. The total relative error of the experiment was $\leq 10\%$.

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 rest steps of the process that makes it possible to reduce the exponent of term $2k_5[\cdot\text{CH}_2\text{OH}]^2$ to 1 in equation $d[\cdot\text{CH}_2\text{OH}]/dt = 0$: $k_6 = \sqrt{2k_5 2k_7}$ and $V_1 = V_5 + 2V_6 + V_7 = (2k_5[\cdot\text{CH}_2\text{OH}] + 2k_7[\cdot\text{CHO}])^2$ [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 percent of the total 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 ethanediol 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 ethanediol formation is $25 \pm 3 \text{ kJ mol}^{-1}$.

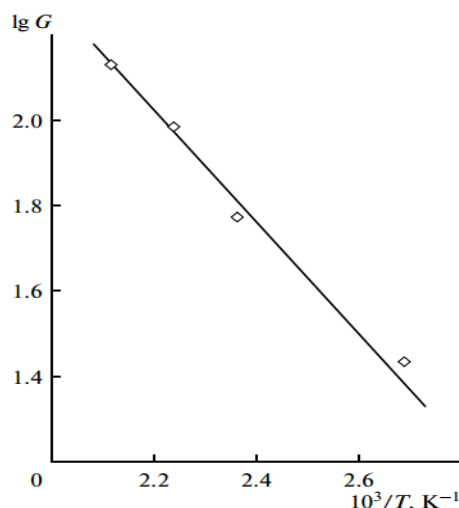


FIGURE 1: Logarithm of the ethylene glycol yield G (molecule/100 eV) versus inverse temperature for the γ -radiolysis of the methanol–formaldehyde (0.9 mol dm^{-3}) system [1].

Figure 2 plots the ethanediol 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 ($144 \text{ mol} \times 10^{-7} \text{ J}$) 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 ($\text{CH}_2=\text{O}$) for reacting with the adduct radical $\text{HOCH}_2\text{CH}_2\text{O}^\bullet$.

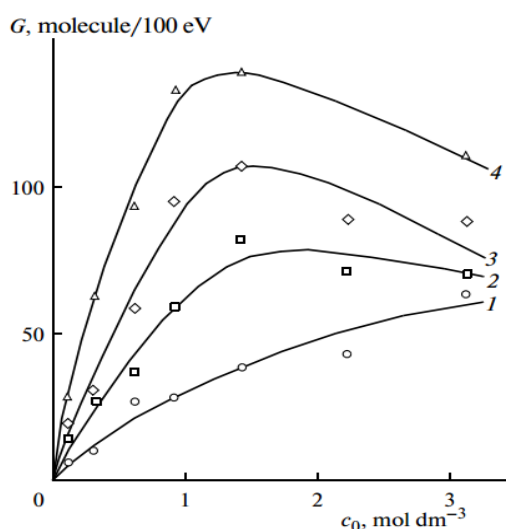


FIGURE 2: Ethylene glycol yield G as a function of the total formaldehyde concentration c_0 for the γ -radiolysis of the methanol–formaldehyde system at $T = 373$ (1), 423 (2), 448 (3), and 473 (4) K [6].

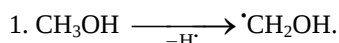
The main by-product of γ -radiolysis in the methanol–formaldehyde system is methylal, $\text{CH}_2(\text{OCH}_3)_2$, which results from the thermal acetalization of formaldehyde. The second most abundant by-product is methyl format, CH_3OCHO , which also

results from the thermal reversible 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}).

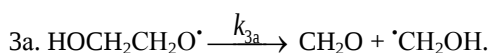
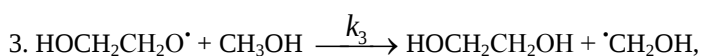
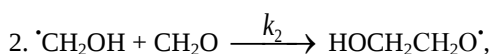
The kinetics of the initiated non branched-chain addition of 1-hydroxyalkyl radicals to free (unsolvated) formaldehyde $\text{CH}_2=\text{O}$ in the γ -radiolysis of saturated aliphatic alcohol-formaldehyde systems, which yields vicinal glycols, carbonyl compounds, and methanol via a chain mechanism, 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.

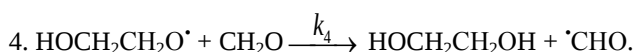
Chain initiation



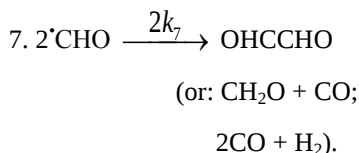
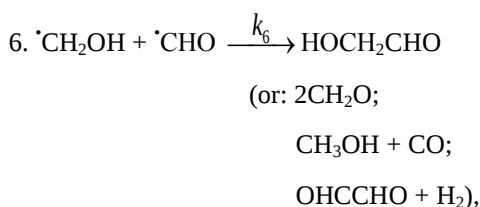
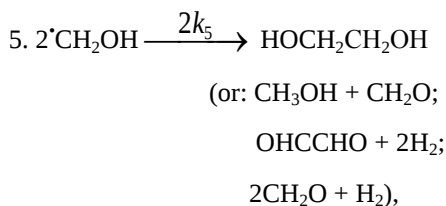
Chain propagation



Inhibition



Chain termination

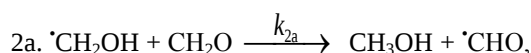


In these reactions, $\cdot\text{CH}_2\text{OH}$ is the reactive hydroxymethyl radical (addend), $\text{HOCH}_2\text{CH}_2\text{O}^\bullet$ is the reactive hydroxyethoxyl radical (adduct), $\cdot\text{CHO}$ is the low-reactive formal radical (inhibitor), $\text{HOCH}_2\text{CH}_2\text{OH}$ is ethanediol, HOCH_2CHO is glycolaldehyde, and OHCCHO glycol is glyoxal. Of the above molecular products, only ethanediol 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 ethanediol through the dimerization of the hydroxymethyl chain carrier radical. The disproportionation of this radical can be neglected [11].

The possible abstraction reaction



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 $\cdot\text{CH}_2\text{OH}$. Besides, it is in essential 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 ($\text{CH}_2=\text{O}$) in the system. The addition of the adduct radical $\text{HOCH}_2\text{CH}_2\text{O}\cdot$ to formaldehyde at elevated temperatures seems unlikely because it would yield an ether linkage.

The hydroxyethoxyl adduct radical $\text{HOCH}_2\text{CH}_2\text{O}\cdot$ resulting from reaction 2 must possess an increased energy due to the energy released upon the conversion of the double bond $\text{C}=\text{O}$ into an ordinary bond ($30\text{--}60 \text{ kJ mol}^{-1}$ for the addition of $\text{C}_1\text{--C}_4$ 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, without diffusing in the solution and, accordingly, without participating in radical-radical termination reactions 5–7. A specific feature of the ethanediol 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 $\cdot\text{CHO}$ 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 alkoxy 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 $-24.3 \text{ kJ mol}^{-1}$ [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 $\text{C}\alpha\text{--H}$ bond dissociation energy for the saturated $\text{C}_1\text{--C}_3$ alcohols [14]. As distinct from reactions 3 and 3a, reaction 4 wastes $\text{HOCH}_2\text{CH}_2\text{O}\cdot$ adduct radicals without regenerating the chain-carrier addend radical $\cdot\text{CH}_2\text{OH}$, causing the termination of the kinetic chain through the formation of the low-reactive radical $\cdot\text{CHO}$. Along with the $\cdot\text{CH}_2\text{OH} + \cdot\text{CHO}$ combination reaction 6, reaction 4 inhibits the nonbranched-chain process.

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

$$V_{3,4,5}(\text{CH}_2\text{OH})_2 = V_1 [f(\alpha l + x)k_2x + V_1 2k_5(\alpha l + \beta + x)^2] f^{-2} \quad (1)$$

where $f = k_2x^2 + (\alpha l + \beta + x)\sqrt{2k_5V_1}$; V_1 is the initiation rate, $\text{mol dm}^{-3} \text{ s}^{-1}$; 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 $l = [\text{CH}_3\text{OH}] \gg [\text{CH}_2=\text{O}] = x$; $\alpha = k_3/k_4$ and $\beta = k_{3a}/k_4$ – ratios of the rate constants ($\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) 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 $c_0 = 1.0 \text{ mol dm}^{-3}$ 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.

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	$10^2 x$	$10^2 x_{\text{calc}}$
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

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 $\nu = (V_3 + V_{3a})/V_1$.

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

$$V_{3,4}(\text{CH}_2\text{OH})_2 = \frac{V_1(\alpha l + x)k_2x}{k_2x^2 + (\alpha l + \beta + x)\sqrt{2k_5V_1}}, \quad (3)$$

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 ($k_{3a} = 0$, $\beta = 0$) will further simplify Eq. (3). In this case, the rate constant k_2 will be an effective quantity.

Equation (1) when $k_2x^2 \ll (\alpha l + \beta + x)\sqrt{2k_5V_1}$ (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 :

$$V_{3,4,5} = (V_1/\varphi^2)[(\varphi k_2x/\sqrt{2k_5V_1}) + 1] \quad (4)$$

were $\varphi = 1$ for the ascending portion of the curve and $\varphi = 2$ for the maximum, when $k_2x^2 \cong (\alpha l + \beta + x)\sqrt{2k_5V_1}$.

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 $V_1 = \varepsilon_1 G(\cdot\text{CH}_2\text{OH})P$, where P is the ionizing radiation dose rate, ε_1 is the electron fraction of methanol in the reaction system [18], and $G(\cdot\text{CH}_2\text{OH})$ is the primary yield of the hydroxymethyl chain-carrier radical – initiation yield.

IV. CONCLUSION

The mechanism and kinetics are developed for the initiated non branched-chain formation of ethanediol 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 ethanediol formation rate on the concentration of the free (unsolvated) form of dissolved formaldehyde.

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