

RADIATION
CHEMISTRY

Effect of Temperature on the Yields of Final Products in the γ -Radiolysis of Formaldehyde Solutions in C_1 – C_3 Alkanols

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Abstract—The effect of temperature on the yields of 1,2-alkanediols in the γ -radiolysis of the methanol(or ethanol)–formaldehyde (0.9 M) systems and on the yields of 1,2-alkanediols, carbonyl compounds, methanol, and ethanol in the γ -radiolysis of the 1-propanol(or 2-propanol)–formaldehyde (1 M) systems was studied over the range 373–473 K. It was found that the temperature dependence of the yields of 1,2-butanediol and 2-methyl-1,2-propanediol exhibited maximums at 423 and 373 K, respectively.

The kinetics of the addition of 1-hydroxyalkyl radicals at the double bond of the free (monomeric, unsolvated) form of formaldehyde in the γ -radiolysis of the aliphatic saturated C_1 – C_3 alcohol–formaldehyde systems were considered in [1, 2]. The experimental dependence of the radiation-chemical yields of final (stable) addition products (1,2-alkanediols and aldehydes, which were formed via a chain mechanism) on the concentration of the free form of formaldehyde was given for formaldehyde solutions in ethanol at 413 and 443 K and in 1-propanol at 413 K. This dependence exhibits a maximum, which is shifted toward lower formaldehyde concentrations with temperature. Silaev and Bugaenko [1, 2] related this behavior to competition between alcohol and free formaldehyde for an adduct radical and to an increase in the concentration of the free formaldehyde form with temperature.

In this work, we present the experimental dependence of the yields of final products formed in the γ -radiolysis of 0.9 and 1 M formaldehyde solutions in methanol, ethanol, 1-propanol, and 2-propanol at 373, 423, 448, and 473 K, respectively.

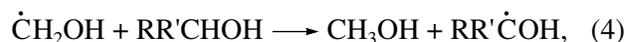
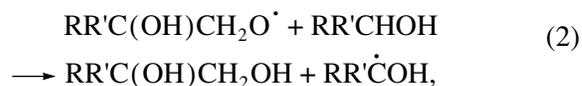
EXPERIMENTAL

The alcohol–formaldehyde solutions were prepared by saturating reagent-grade alcohols with formaldehyde vapor in a nitrogen flow. The formaldehyde vapor was released by the decomposition of chemically pure paraformaldehyde in a vessel placed in an oil thermostat at 403 K. The concentration of formaldehyde in solution was determined by the sulfite method [3]. The experimental procedure with the use of ⁶⁰Co γ -radiation and the gas-chromatographic analysis final products were described elsewhere [4]. The dose rate was 6.9 Gy/s, as determined using a ferrous sulfate dosime-

ter; the absorbed dose range was $(1.25$ – $8.84) \times 10^4$ Gy with consideration for the electron densities of alcohols. The overall relative experimental error was $\leq 10\%$.

RESULTS AND DISCUSSION

In the γ -radiolysis of alcohol–formaldehyde systems, the resulting 1-hydroxyalkyl radicals are attached to the carbon atoms of the free form of formaldehyde, i.e., the unsolvated formaldehyde molecule, which is chemically unbound to the solvent, in solution [3]. At room temperature, the concentration of this formaldehyde species in alcohols is as low as a few fractions of percent of the total formaldehyde concentration (of free and solvated formaldehyde species), and it increases with temperature in accordance with an exponential law [3]. According to published data [5], the effective activation energies of formaldehyde desolvation are 59 ± 5 kJ/mol in methanol or ethanol and 46 ± 4 kJ/mol in 1-propanol or 2-propanol at a total formaldehyde concentration of 1 mol/l in solution. The addition process includes the following fragment of a reaction scheme [6]:



where R is H, CH₃, or C₂H₅; R' is H or CH₃; RR' $\dot{C}OH$ is a 1-hydroxyalkyl radical; RR'C(OH)CH₂O \cdot is an adduct radical; RR'CHOH is an alcohol;

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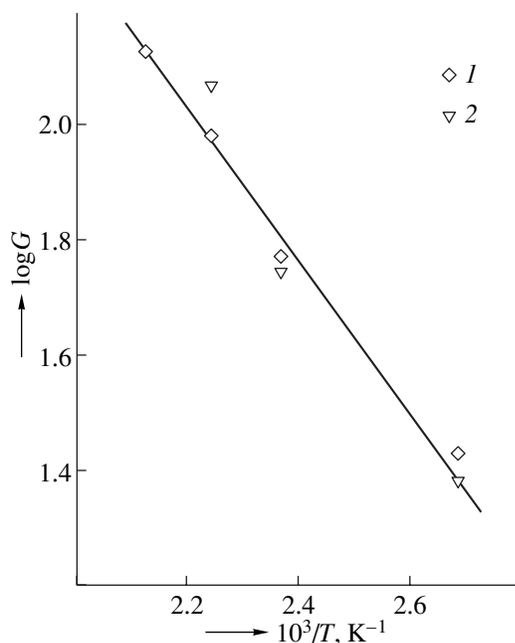


Fig. 1. Logarithmic yields G (molecule/100 eV) of (1) ethanediol and (2) 1,2-propanediol versus the reciprocal of temperature T in the γ -radiolysis of the methanol–formaldehyde (0.9 M) and ethanol–formaldehyde (0.9 M) systems, respectively.

$RR'C(OH)CH_2OH$ is a 1,2-alkanediol; and $RR'CO$ is an aldehyde or ketone.

In the case of the methanol–formaldehyde system, reaction (3) is the reverse step of reaction (1), whereas reaction (4) is canceled. In the case of the other (non-methanol) alcohol–formaldehyde systems, the mechanism of reaction (3) of the degradation of an adduct radical to form a carbonyl compound includes the formation of an internal hydrogen bond $H\cdots O$ and isomerization [1, 2]. The probability of occurrence of this reaction should increase with temperature. The hydroxymethyl radical formed in reaction (3) enters into a dimerization reaction with an analogous radical in the bulk of solution to give ethanediol. A 1,2-alkanediol and methanol are formed in reactions (2) and (4), respectively, and initial 1-hydroxyalkyl radicals, which participate in addition reaction (1) with formaldehyde, are regenerated.

Figure 1 demonstrates the Arrhenius plots of the yields of ethanediol and 1,2-propanediol in the γ -radiolysis of 0.9 M formaldehyde solutions in methanol and ethanol, respectively. As the temperature was elevated from 373 to 473 K, the concentration of the free formaldehyde species, which was calculated from published data [5], increased from 2.78×10^{-3} to 0.16 mol/l in methanol or from 3.50×10^{-3} to 0.21 mol/l in ethanol. The effective activation energy of 1,2-alkanediol formation was 25 ± 3 kJ/mol.

Figures 2 and 3 demonstrate the dependence of the product yields on temperature and the corresponding

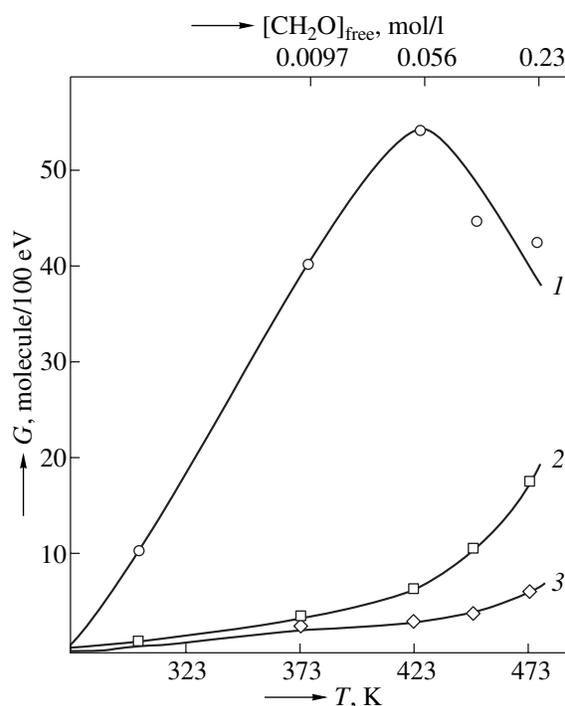


Fig. 2. Dependence of the yields G of (1) 1,2-butanediol, (2) propanol, and (3) ethanediol on the temperature T and the corresponding concentration $[CH_2O]_{\text{free}}$ of free formaldehyde species [5] in the γ -radiolysis of the 1-propanol–formaldehyde (1 M) system. Data for 303 K were borrowed from [7].

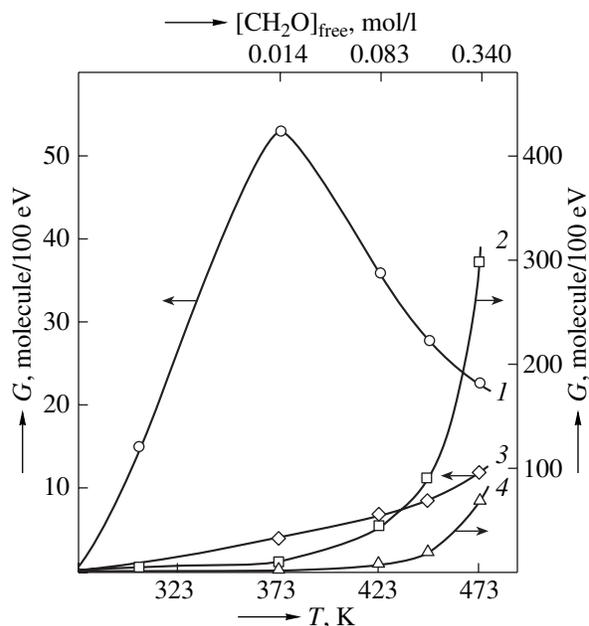


Fig. 3. Dependence of the yields G of (1) 2-methyl-1,2-propanediol, (2) propanone, (3) ethanediol, and (4) methanol on the temperature T and the corresponding concentration $[CH_2O]_{\text{free}}$ of free formaldehyde species [5] in the γ -radiolysis of the 2-propanol–formaldehyde (1 M) system. Data for 303 K were borrowed from [7].

Effective activation energies $E_{a, \text{eff}}$ of the formation of final products in the γ -radiolysis of the 1-propanol (or 2-propanol)-formaldehyde system

No.	Product*	Temperature range, K	$E_{a, \text{eff}}$, kJ/mol
1	1,2-Butanediol	303–423	15 ± 2
2	Propanal	423–473	33 ± 4
3	Ethanediol	423–473	23 ± 3
4	2-Methyl-1,2-propanediol	303–373	17 ± 2
5	Propanone	373–473	47 ± 6
6	Ethanediol	373–473	16 ± 2
7	Methanol	373–473	46 ± 6

* Products 1–3 and 4–7 refer to the 1-propanol-formaldehyde and the 2-propanol-formaldehyde system, respectively.

concentration of the free formaldehyde species [5] in the γ -radiolysis of 1 M formaldehyde solutions in 1-propanol and 2-propanol. The yields of 1,2-alkanediols and carbonyl compounds at 303 K are given as reported in [7]. In the 1-propanol-formaldehyde system, the yield of methanol (16.4 molecule/100 eV) was determined only at 473 K. The temperature dependence of the yields of 1,2-alkanediols exhibits a maximum. The yields of other products exponentially increase with temperature (table). The table summarizes the primary estimates of the effective activation energy for the formation of final products in the γ -radiolysis of the 1-propanol (or 2-propanol)-formaldehyde systems. These estimates were made by treating the linear portions of Arrhenius plots for these systems with the least-squares technique.

Based on the data presented in Figs. 1–3 and the mechanism proposed [1, 2] for the generation of final products in 1,2-alkanediol formation reaction (2) and in parallel (competitive) reaction (3) of the formation of a carbonyl compound as a result of the degradation of an adduct radical, we may conclude that the thermal stability of this radical decreases with increasing number of carbon atoms in its structure and with increasing the degree of branching. The adduct radical in a 0.9 M formaldehyde solution in ethanol is thermally stable up to 473 K, whereas the thermal dissociation of this radical in 1 M formaldehyde solutions in 1-propanol and 2-propanol comes into play even at 423 and 373 K, respectively (maximums in the plots in these temperature regions). This is indicative of a relatively lower thermal stability of the adduct radical in the 2-propanol-formaldehyde system.

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