

SHORT COMMUNICATIONS
Radiation Chemistry

Dependence of 1,2-Propanediol Yield on Formaldehyde Concentration in γ -Radiolysis of Ethanol–Formaldehyde System at 373–473 K

A. I. Novoselov, M. M. Silaev, and L. T. Bugaenko[†]

Moscow State University, Moscow, 119992 Russia

e-mail: mmsilaev@rc.chem.msu.ru

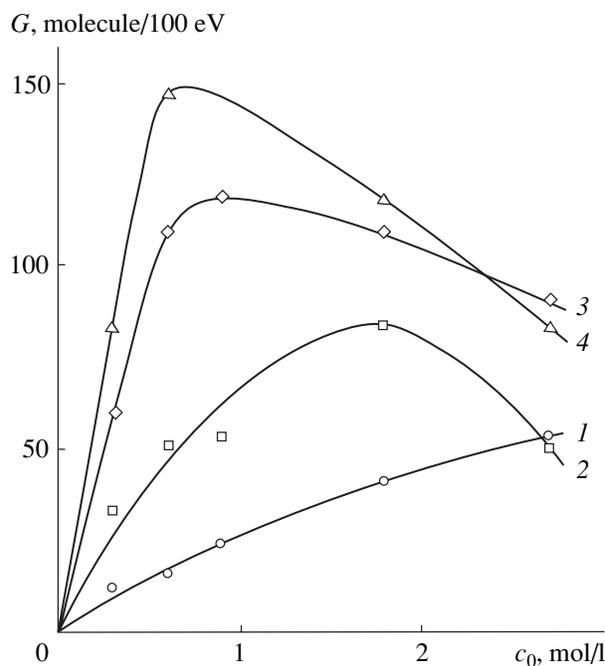
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In earlier reports, the kinetics of addition of 1-hydroxyalkyl radicals to the carbonyl carbon of the free (unsolvated monomer) form of formaldehyde during the liquid-phase γ -radiolysis of saturated aliphatic C₁–C₃ alcohol–formaldehyde systems, which resulted in the formation of 1,2-alkanediols via the chain mechanism, was discussed [1–3]. The influence of temperature on these processes was considered in [4]. In this paper, we present the experimentally determined dependence of the yield of 1,2-propanediol on the total concentration of formaldehyde including the concentrations of both the free form of dissolved formaldehyde and the form chemically bound with alcohol [5]. The experimental procedure using the sealed-ampoule technique with freeze–pump–thaw cycling employed to degas liquid samples and the GLC analysis for stable products were described in [4, 6]. The dose rate of ⁶⁰Co γ -radiation determined with a ferrous sulfate dosimeter was 6.9 Gy/s, the range of doses absorbed by solution with allowance for the electron density of ethanol was $(1.76\text{--}8.82) \times 10^4$ Gy. The total relative error of the experiment was $\leq 10\%$.

The figure shows the dependence of 1,2-propanediol yields on the total concentration of formaldehyde (0.3, 0.6, 0.9, 1.8, and 2.7 mol/l) in the ethanol–formaldehyde system at temperatures of 373, 423, 448, and 473 K. The maximum yield of the product reaches 147 molecule/100 eV at 473 K and a 0.6 mol/l formaldehyde concentration in ethanol. The concentration plot of the yields at 373 K has no maximum at whatever concentration of formaldehyde (including its upper value of 2.7 mol/l used), whereas the curves for temperatures of 423, 448, and 473 K pass through a maximum in the concentrations range of 0.6–1.8 mol/l, with the peak value shifting to lower formaldehyde concentrations with an increase in temperature. The appearance

of a maximum on these curves was associated [1–3] with the competition between alcohol and formaldehyde in the free form CH₂=O for the radical adduct CH₃CH(OH)CH₂O[•], and its shift to lower concentrations with temperature was attributed to an increase in the concentration of the free form of formaldehyde in the solution according to the exponential law with a rise in temperature [7].



Radiation-chemical yield G of 1,2-propanediol as a function of the total concentration c_0 of formaldehyde during the γ -radiolysis of the ethanol–formaldehyde system at temperatures of 373 (1), 423 (2), 448 (3), and 473 (4) K.

[†] Deceased.

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