

Addition of 1-Hydroxyalkyl Free Radicals to Unsolvated Formaldehyde in Alcohol Formaldehyde Solutions with Nonbranched-Chain Formation of 1,2-Alkanediols

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Abstract: A mechanism of the initiated nonbranched-chain process of forming 1,2-alkanediols and carbonyl compounds in alcohol–formaldehyde systems is suggested. 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 unsolvated formaldehyde. The experimental concentration of the free unsolvated form of formaldehyde are given at the different temperatures, solvent permittivity, and total concentrations of formaldehyde in water and alcohols. An empirical equation for calculating the free formaldehyde concentration in alcohol–formaldehyde (including water/ethanediol–formaldehyde) systems at various temperatures and total formaldehyde concentrations and an equation for evaluating solvent concentrations in these systems were derived.

Keywords: nonbranched-chain process, free formaldehyde, 1-hydroxyalkyl radical, formyl radical, competing reaction, equation.

1. INTRODUCTION

Free radicals add to the carbon atom at the double bond of the carbonyl group of dissolved free (unsolvated, monomer) formaldehyde. The concentration of free formaldehyde in the solution at room temperature is a fraction of a percent of the total formaldehyde concentration, which includes formaldehyde chemically bound to the solvent [1]. The concentration of free formaldehyde exponentially increases with increasing temperature [2]. The energy released as a result of this addition, when the C=O bond is converted into an ordinary bond, is 30 to 60 kJ mol⁻¹ (according to the data on the addition of C1–C4 alkyl radicals in the gas phase under standard conditions □3–6□). The resulting free 1:1 adduct radicals can both abstract hydrogen atoms from the nearest-neighbor molecules of the solvent or unsolvated formaldehyde and, due to its structure, decompose by a

monomolecular mechanism including isomerization [7, 8]. The analysis of stable liquid-phase products was carried out by the gas chromatographic method. The quasi-steady-state treatment is used to obtain kinetic equations.

Addition of 1-Hydroxyalkyl Free Radicals with Two or More Carbon Atoms

Free 1-hydroxyalkyl radicals (which result from the abstraction of a hydrogen atom from the carbon atom bonded to the hydroxyl group in molecules of saturated aliphatic alcohols but methanol under the action of chemical initiators [9, 10], light [11, 12], or ionizing radiation [13, 14]) add at

the double bond of free formaldehyde dissolved in the alcohol, forming 1,2-alkanediols [7–10, 12–18], carbonyl compounds, and methanol [14, 15] via the chaining mechanism. (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 on the polarity of the solvent [2, 14]. For the □-radiolysis of 1(or 2)-propanol–formaldehyde system at a constant temperature, the dependences of the radiation-chemical yields of 1,2-alkanediols and carbonyl compounds as a function of the formaldehyde concentration show maxima and are symbatic [13, 15]. For a constant total formaldehyde concentration of 1 mol dm⁻³, the dependence of the 1,2-alkanol yields as a function of temperature for 303–473 K shows a maximum, whereas the yields of carbonyl compounds and methanol increase monotonically [14] (along with the concentration of free formaldehyde [2]). In addition to the above products, the nonchain mechanism in the □-radiolysis of the solutions of formaldehyde in ethanol and 1- and 2-propanol gives ethanediol, carbon monoxide, and hydrogen in low radiation-chemical yields (which, however, exceed the yields of the same products in the □-radiolysis of individual alcohols) [7, 14, 15]. The available experimental data can be described in terms of the following scheme of reactions.