

RADIATION
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Applied Aspects of the γ -Radiolysis of C_1 – C_4 Alcohols and Binary Mixtures on Their Basis

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Abstract—Generalized data on the γ -radiolysis of aliphatic C_1 – C_4 alcohols are summarized. These data can be used for solving practical problems in the related areas of research. In particular, a rate equation that relates the radiation-chemical yield of an 1 : 1 adduct formed from saturated and unsaturated components upon the γ -radiolysis of a binary system to the concentrations of these components was derived. An equation was obtained for estimating the reaction rate constants of decay of identical hydroxyalkyl radicals in collisions with each other from the reciprocal viscosity (fluidity) of corresponding alcohols. An empirical equation for calculating the concentration of the free (desolvated) form of formaldehyde in alcohol–formaldehyde systems at various temperatures and total formaldehyde concentrations and an equation for evaluating solvent concentrations in these systems were derived.

A wealth of data on the γ -radiolysis of both individual aliphatic C_1 – C_4 alcohols and binary mixtures on their basis has been obtained [1–4]. Thus, the experimental data obtained in studying alcohols can be used to solve scientific problems in other research areas. The competitive kinetics of free-radical addition to the double bonds of molecules with the formation of 1 : 1 adducts and inhibition by an unsaturated substrate [5] was developed. The applicability of this kinetics to radical chain oxidation processes was demonstrated [6]. In this work, the general results that can be used to rapidly solve practical problems in related areas of research are considered.

Table 1 presents the bond energies of alcohol molecules, which are required for the preliminary estimation of the probabilities of many radiolytic processes occurring in alcohol systems.

Data on the γ -radiolysis of aliphatic monohydric C_1 – C_3 alcohols and 2-methyl-2-propanol over a wide temperature range of 195–503 K were summarized earlier [1], allowing their relative radiation and thermal stability to be determined. Such data may be of importance for the prediction of radiolytic transformations in both individual alcohols that have not been studied and various mixtures of previously examined alcohols with any components at different temperatures. Figure 1 demonstrates the logarithms of the total yields of decomposition of C_1 – C_3 alcohols upon γ -radiolysis as functions of the reciprocal temperature. Published in the cited paper [1] were also the apparent activation energies of the following radiolytic processes in alcohols: alcohol decomposition; formation of the products of C_α –C and C–O bond cleavage; and formation of α -diols (by the colligation of α -hydroxyalkyl radicals, the products of C_α –H bond cleavage in alcohols) at low

temperatures (≤ 293 K) when thermal degradation does not occur. The values of $E_{a(\alpha\text{-diol})}$ (which are equal to 1.3, 5.7, 2.7, and 4.4 kJ/mol for methanol, ethanol, 1-propanol, and 2-propanol, respectively) can be used in the Arrhenius equation [10] for extrapolating the initial radiation-chemical yields of α -hydroxyalkyl radicals in alcohols (these yields at room temperature are known from EPR data [11]) to higher temperatures. The addition of γ -hydroxyalkyl radicals to olefins and their derivatives in α -radiolysis resulted in the chain formation of molecular products, primarily, 1 : 1 adducts [3–5]. It was experimentally found that, in accordance with increasing reactivity of saturated alcohols in the forma-

Table 1. Bond energies (kJ/mol) in alcohols in the gas phase at 298 K [7]

Alcohol	Bond type			
	C_α –C	C_α –H	C–O	O–H
Methanol	–	383.7	383.3	428.4
Ethanol	356.1	377.4	381.2	424.7
2-Propen-1-ol	363.6	330.1 ^a	334.7 ^{a,b}	
1-Propanol	342.7	381.2 ^a	382.8	427.2
2-Propanol	339.3	379.1	389.1	437.6
2-Methyl-2-propanol	310.0 ^c	–	387.9	434.3

Note: ^a Calculated from data [7] using the ratio between similar bond energies in the series of ROH/RX pairs (where R is a saturated or unsaturated C_1 – C_3 hydrocarbon radical, and X is the CH_3 or OCH_3 group in the case of C_α –H or C–O bonds, respectively). For each type of bonds in this series, these ratios were constant to within relative deviations, which were no higher than 2 or 8% in the cases of C_α –H or C–O bonds, respectively.
^b According to data [8].
^c According to data [9].

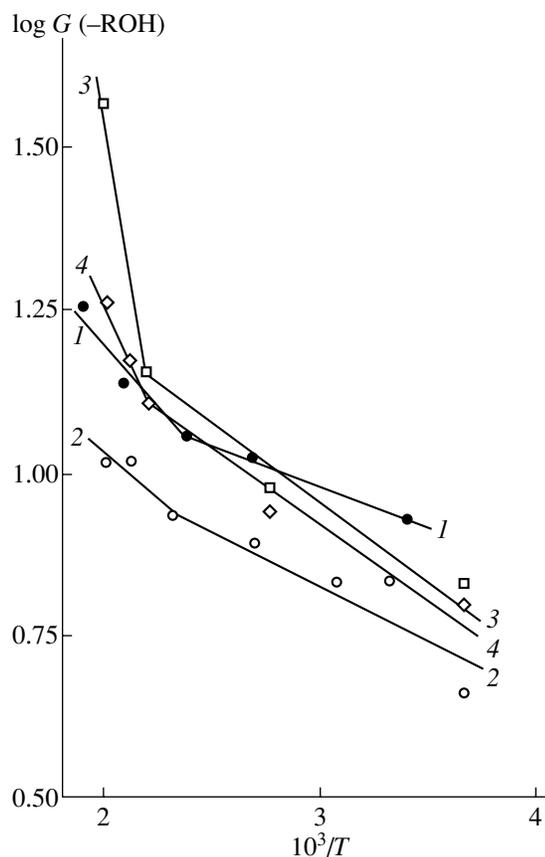


Fig. 1. Logarithms of the yields of alcohol decomposition $G(-ROH)$, molecule/100 eV, as functions of the reciprocal temperature $1/T$, K^{-1} , in the γ -radiolysis of (1) methanol, (2) ethanol, (3) 1-propanol, and (4) 2-propanol.

tion of γ -diols upon the γ -radiolysis of 2-propen-1-ol solutions in saturated C_1-C_3 alcohols [3] (Fig. 2), as well as in the formation of combination α -diols upon the γ -radiolysis of individual saturated C_1-C_3 alcohols in a low-temperature region (up to a changeover to the radiation-thermal mode [1]), the alcohols can be arranged in the order methanol < 1-propanol < ethanol < 2-propanol. This order is inverted with respect to the homologous series.¹ It was demonstrated [4] that this order directly correlates with the order of parameters that reflect the macroscopic (structural) properties of a medium, such as the entropy ΔS_{298}° of formation of hydrogen bonds in alcohols (this entropy quantitatively characterizes the association of alcohols) and the energy $E_{\lambda m}$, which corresponds to the wavelength at an optical absorption band maximum of solvated electrons in alcohols (i.e., the energy of solvation). The above order inversely correlates with the sequence of the apparent activation energies E_D of the self-diffusion of alcohols (Table 2).

¹ A similar order was obtained by Zamyslov [12] in the study of 3,3,3-trifluoro-1-propene telomerization with saturated alcohols under exposure to γ -radiation at 303 K.

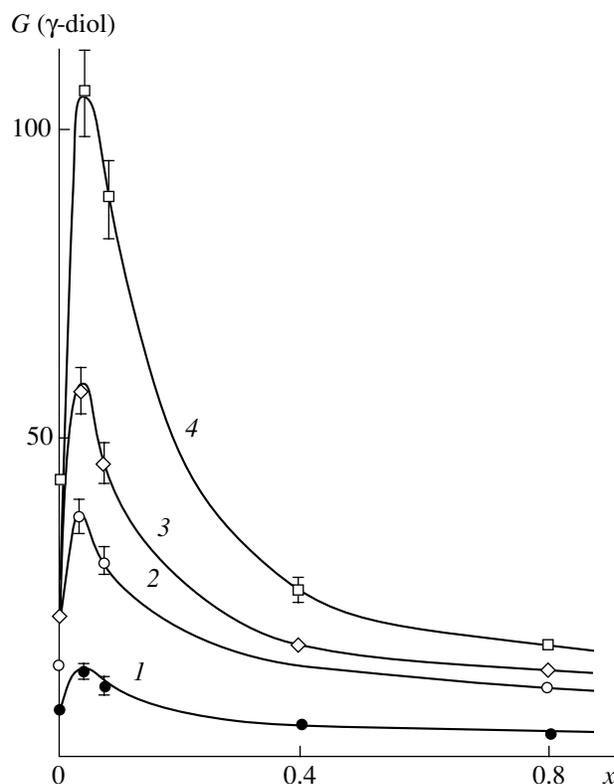


Fig. 2. Yields G (molecule/100 eV) of (1) 1,4-butanediol, (2) 1,4-hexanediol, (3) 1,4-pentanediol, and (4) 2-methyl-2,5-pentanediol as functions of the initial concentration x (mol/dm^3) of 2-propen-1-ol in (1) methanol, (2) 1-propanol, (3) ethanol, and (4) 2-propanol, respectively, at 433 K.

The curves of the radiation-chemical yields of γ -diols (molecular products of the addition of α -hydroxyalkyl radicals to 2-propen-1-ol [3]), as well as 1 : 1 adducts resulted from the addition of any other saturated free radicals to olefins [13], plotted against the concentration of an unsaturated compound exhibit a maximum. Previously [6, 14, 15], based on the proposed scheme with competitive reactions (i.e., parallel reactions in which the molecules of both saturated and unsaturated reactants compete for an adduct radical), the following rate equation with one parameter α subject to direct determination was derived using a quasi-steady-state approximation to fit to nonmonotonic functions of this kind:

$$G(1 : 1\text{-adduct}) = \frac{\varepsilon G(R_{\text{sat}})\alpha l x}{x^2 + (\alpha l + x)x_m^2/\alpha l_m}, \quad (1)$$

$$k_{\text{add}} = \alpha l_m [2k\varepsilon G(R_{\text{sat}})P]^{0.5}/x_m^2,$$

where ε is the electron fraction of the saturated component; $G(R_{\text{sat}})$ is the initial radiation-chemical yield of α -hydroxyalkyl or other saturated free radicals (the yield of initiation); P is the dose rate; l and x are the initial

Table 2. Apparent activation energies E_a of the formation of α -diols in the γ -radiolysis of saturated C_1 – C_3 alcohol–2-propan-1-ol systems and various parameters that characterize the structural properties of the medium

Alcohol	Parameter			
	E_a [4], kJ/mol	ΔS_{298}° [16], J mol ⁻¹ K ⁻¹	$E_{\lambda m}$ [17]	E_D [18]
			kJ/mol	
Methanol	27.5	-35.8	191	11.6
1-Propanol	22.6	-61.1	188	17.8
Ethanol	19.5	-63.6	176	19.3
2-Propanol	14.4	-79.9	147	22.2

molar concentrations of saturated and unsaturated parent components, respectively ($l > x$); l_m and x_m are the values of l and x at the point of a maximum in the curve; α is the ratio between the rate constants of competitive reactions; and $2k$ is the rate constant of decay of identical chain-carrier saturated free radicals on collisions with each other. Equation (1) describes the dependence (with a maximum) of the radiation-chemical yield (or formation rate) of an 1 : 1 adduct on the concentration of the unsaturated component in binary mixtures containing a saturated and an unsaturated component in commensurable concentrations; it also describes the yields (formation rates) of a peroxide and an alcohol (with the same number of carbon atoms as in the parent hydrocarbon) as functions of the concentration of molecular oxygen in uncatalyzed oxidation by an unbranched radical chain mechanism (when the yields of these products are much higher than the yields of carbonyl compounds). The reaction rate constant k_{add} of free-radical addition to a double bond can also be determined using Eq. (1).

The reaction rate constants $2k$ of the mutual (diffusion-controlled) decay of identical hydroxyalkyl radicals from alcohols appear in many rate equations that relate the formation rates of alcohol-based products to the reactant concentrations. Figure 3 demonstrates the linear dependence of the experimental rate constants of decay of C_2 and C_3 free hydroxyalkyl radicals in individual alcohols in a neutral medium at room temperature, the decay constants derived from the experimental self-diffusion coefficients of C_1 – C_4 alcohols, and the one-half values² [10] of the experimental decay rate constants of C_2 – C_4 hydroxyalkyl radicals in 0.1 M aqueous alcohol solutions with pH 6 (12 values altogether) on the reciprocal viscosity (fluidity) of corresponding alcohols (the correlation coefficient is 0.995). This dependence makes it possible to numerically eval-

uate the unknown values of the above constants using the following equation of a straight line passing through the origin:

$$2k = aD = b_{\text{expt}}/\eta, \quad (2)$$

where $a = (1.0 \pm 0.13) \times 10^{15}$ m/mol is a coefficient from the Smoluchowsky equation for identical species, saturated C_1 – C_4 alcohols, at 298 K [20]; D is the self-diffusion coefficient, m²/s; $b_{\text{expt}} = (1.27 \pm 0.05) \times 10^3$ N m mol⁻¹; and η is the viscosity, 10⁻³ N s m⁻² or MPa s [10]. The use of the empirical coefficient b_{expt} reduces differences between the estimated and experimental (taken as 100%) average values of both the self-diffusion coefficients of alcohols $D = b_{\text{expt}}/a\eta$ and the decay rate constants $2k$ of hydroxyalkyl radicals to values insignificant in comparison with the relative measurement error ($\leq 20\%$). It is only for the ethanol self-diffusion coefficient and the decay rate constant of hydroxymethyl radicals that the difference between their calculated and experimental values is 12.5 and 18%, respectively.

The decay rate constants $2k$ of identical hydroxyalkyl radicals at a given temperature can be determined from analogous room-temperature constants by the Arrhenius equation with the use of the known activation energies E_a of these reactions. For the majority of alcohols, these values of E_a are approximately equal to the corresponding activation energies of self-diffusion E_D or viscous flow E_η to within the experimental error [10]. The values of E_η were calculated earlier [10] for the majority of aliphatic C_1 – C_8 alcohols from the slopes of the logarithms of the viscosities plotted as linear functions of the reciprocal temperature over the range 273–373 K.

The addition of α -hydroxyalkyl radicals to the carbon atom at the double bond of the free (desolvated, monomeric) formaldehyde molecule under the action of γ -radiation resulted in the chain formation of α -diols [5, 12]. In these processes, the desolvation of formaldehyde in alcohol–formaldehyde solutions can play a crucial role in the reactivity of alcohols. Neutral formaldehyde solutions in alcohols at room temperature primarily consist of a mixture of formaldehyde polymer solvates reversibly bound to alcohols; these polymer solvates differ in molecular mass and have the general formula $RO(CH_2O)_nH$, where $n = 1$ – 4 [22]. The concentration of formaldehyde that occurs in solution as a free, desolvated active species chemically unbound to the solvent (this species is capable of scavenging free radicals) at room temperature is lower than a percent of the total formaldehyde concentration [22]. The concentration of the free formaldehyde species in solutions was determined by high-temperature spectrophotometry in the range 335–438 K at total formaldehyde concentrations (free and bound species including the concentration of polymer solvates) of 1.0–8.4 mol/dm³ in water, ethanediol, methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol [23]. This concen-

² In this case, the use of k values in place of $2k$ is associated with a lower viscosity of aqueous alcohol solutions and with higher values of the diffusion coefficients of alcohol molecules in them [19, 20]; these values are almost equal to the diffusion coefficients of corresponding hydroxyalkyl radicals [10].

tration increases with temperature according to an exponential law, and it can be as high as a few percent of the total concentration in solution under the test conditions, up to 19.3% in the case of 2-methyl-2-propanol at a total concentration of 1.0 mol/dm³ and a temperature of 398 K (Fig. 4). The following empirical equation relating the concentration x (mol/dm³) of free formaldehyde to temperature T (K) and the total concentration c_0 in solution (measured at room temperature), was developed by the treatment of 101 data points:

$$\log x = -\alpha(10^3/T) + \beta + \gamma \log c_0, \quad (3)$$

where the coefficients α and β were calculated as the parameters of a straight-line equation by the least-squares technique from the dependence of $\log x$ on $1/T$ at $c_0 = 1.0$ mol/dm³ for various solvents, and the coefficient γ was obtained as the average value of the slopes of $\log x$ as linear functions of $\log c_0$ at various series of fixed temperatures. Table 3 summarizes these coefficients for each solvent. As regards the experimental data, the error in the calculations of the concentration x of free formaldehyde made by Eq. (3) in the specified temperature range was no higher than 25%.

On the assumption that the dependence of the density of a given solution on the concentration of formaldehyde is similar to the analogous linear dependence found for aqueous formaldehyde solutions (0–14 mol/dm³; 291 K) [24], the concentrations l_T (mol/dm³) of alcohols in alcohol–formaldehyde solutions at a certain temperature can be estimated by the equation

$$l_T = \frac{(10^3 d - 21.6 c_0) d_T}{(d + 8.4 \times 10^{-3} c_0) M}, \quad (4)$$

where c_0 is the total formaldehyde concentration (mol/dm³); M is the molecular mass (g/mol) of the solvent; d and d_T are the solvent densities (g/cm³) at room and given temperatures, respectively; the coefficients 8.4×10^{-3} and 21.6 have the units of 10³ g/mol and g/mol, respectively. Earlier [23], it was found that the concentration of the free formaldehyde species decreased with the solvent permittivity at a constant temperature (Fig. 4). Water is an exception. Although water is more polar than alcohols, the concentration of formaldehyde in an aqueous solution is anomalously high and reaches the level of its concentration in 2-propanol, all other factors being the same (Fig. 4). This can be due to the specific instability of hydrated formaldehyde species and the ease of their conversion into free formaldehyde with increasing temperature. Consequently, it may be expected that the addition of a less polar solvent to an alcohol having a higher polarity (as well as the addition of water to methanol or ethanol) will be equivalent to an increase in temperature with respect to an increase in the concentration of the free form of dissolved formaldehyde.

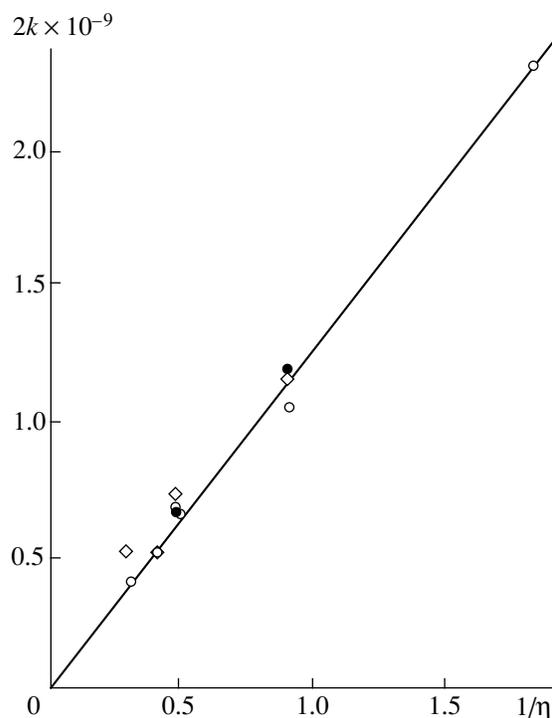


Fig. 3. Reaction rate constants $2k$ (dm³ mol⁻¹ s⁻¹) of hydroxyalkyl radical decay in individual C₁–C₄ alcohols at room temperature as functions of the reciprocal viscosity $1/\eta$ (MPa s)⁻¹ of these alcohols: (●) $2k_{\text{expt}}$, (○) $2k = aD$, and (◇) $2k = k_{0,1} M$.

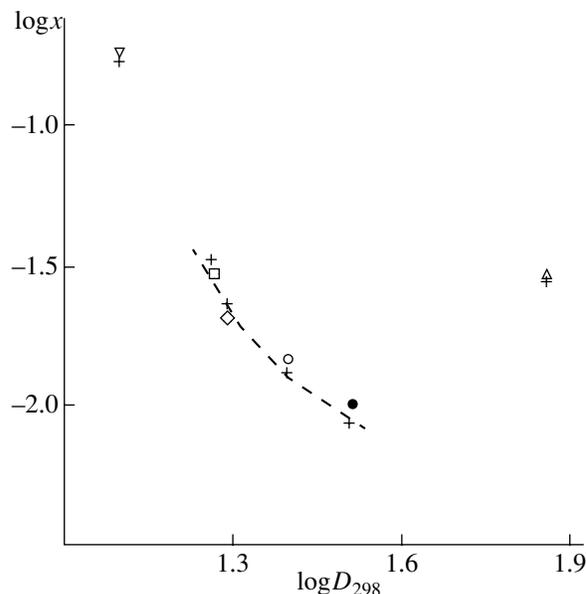


Fig. 4. Logarithmic plot of the experimental concentrations x (mol/dm³) of free formaldehyde at its total concentration $c_0 = 1.0$ mol/dm³ and 395 ± 3 K in (Δ) water, (●) methanol, (○) ethanol, (◇) 1-propanol, (□) 2-propanol, and (▽) 2-methyl-2-propanol as functions of the permittivity D_{298} of these solvents (+ refers to the concentrations x in the above solvents calculated by empirical Eq. (3)).

Table 3. Coefficients of empirical Eq. (3) for the estimation of the concentration x of the free formaldehyde species in polar solvent–formaldehyde systems [23]

Coefficient	Solvent		
	α	β	γ
Water	2.36	4.45	0.80
Ethanediol	1.83	2.60	1.28
Methanol	3.11	5.58	$0.22 c_0/\log c_0$
Ethanol	3.10	5.92	$1.10 (10^3/T) - 1.44$
1-Propanol	2.42	4.47	1.30
2-Propanol	2.42	4.64	1.05
2-Methyl-2-propanol	3.19	7.31	0.96

In summary, the material presented in this paper makes it possible to rapidly evaluate the radiation and thermal stability of C_1 – C_3 alcohols (Fig. 1). It explains the reactivity order, which is inverted with respect to the homologous series of alcohols, in the discussed processes (Table 2). Under certain conditions, an overall rate equation can be derived for unbranched radical chain addition and oxidation reactions whose experimental rate curves exhibit a maximum (Eq. (1)). Based on the above considerations, the rate decay constant of free hydroxyalkyl radicals can be calculated from the known self-diffusion coefficients or viscosities of an alcohol (Eq. (2); Fig. 3). These constants and the initial yields of α -hydroxyalkyl radicals can be extrapolated to a given temperature if their values are known only for room temperature. The concentration of the free desolvated formaldehyde species in water and C_1 – C_4 alcohols can be estimated at various temperatures and concentrations of dissolved formaldehyde (Eq. (3); Table 3), and the solvent concentration in these solutions can be calculated (Eq. (4)).

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