# MATHEMATICAL SIMULATION OF THE KINETICS OF RADIATION INDUCED HYDROXYALKYLATION OF ALIPHATIC SATURATED ALCOHOLS

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**Abstract**—The paper reports on the development of the kinetics of radiation hydroxymethylation and hydroxypropylation chain processes relating to aliphatic saturated alcohols in the $\gamma$-radiolysis of the alcohol–unsaturated compound systems to give 1,2- and 1,4-diols respectively These processes were simulated mathematically The kinetic curves computed are in good agreement with the experimental dependences The kinetic parameters of the processes, including the rate constants for the addition of $\alpha$-hydroxyalkyl radicals from the saturated alcohols to the double bond of the unsaturated component, viz formaldehyde or 2-propene-1-ol in the systems, were estimated The constants (in $dm^3/mol$ s) for the saturated alcohol–formaldehyde systems incorporating ethanol as the saturated alcohol were found to be $(1\ 5 \pm 0\ 3)\ 10^4$ at 413 K and $(2\ 1 \pm 0\ 5)\ 10^4$ at 443 K, incorporating 1-propanol– $(6\ 0 \pm 1\ 3)\ 10^3$ at 413 K, for the saturated alcohol–2-propene-1-ol systems incorporating methanol, ethanol, 1- and 2-propanol– $(2\ 5 \pm 0\ 3)\ 10^4$, $(6\ 5 \pm 0\ 9)\ 10^4$, $(2\ 7 \pm 0\ 4)\ 10^4$ and $(1\ 0 \pm 0\ 1)\ 10^5$, respectively, at 433 K

## INTRODUCTION

The process of hydroxyalkylation of an aliphatic saturated monohydric alcohol (or diol) with an unsaturated alcohol or carbonyl compound dissolved in it consists in the addition of an $\alpha$-hydroxy-alkyl radical to the double bond of one of these two substances (radicals of this type are mainly formed when hydrogen atoms are abstracted from the primary or secondary saturated alcohol molecules (Asmus *et al*, 1973)), followed by the abstraction of a hydrogen atom from any molecule of the system with the appearing radical-adduct This gives rise to a saturated polyhydric alcohol where the number of hydroxyl groups equals that of the parent alcohol plus one $\alpha$-Hydroxyalkyl radicals can be generated in the system both under the effect of $\gamma$-radiation (Shadyro, 1975, Silaev, 1990), light (Urry *et al*, 1953, 1954) and peroxide initiation (Nikishin *et al*, 1966; Oyama, 1965, Urry *et al*, 1953, 1954) The specific feature of the kinetics of the process consists of the fact that the dependences of the hydroxyalkylation product yield on unsaturated component concentration in the systems pass through a maximum at low concentrations of this component The hydroxyalkylation process occurs in one stage, at elevated temperatures it is controlled by a chain mechanism (Shadyro, 1975, Silaev *et al*, 1986a, 1990) and may be of practical significance.

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†These data were obtained at our Radiation Chemistry Laboratory by A I Novoselov

## MAJOR KINETIC MODELS OF HYDROXYALKYLATION

In the case of hydroxypropylation the $\alpha$-hydroxy-alkyl radical adds to the $\gamma$-carbon atom at the double bond of 2-propene-1-ol, as is typical of all functionally substituted olefins of this type (Dixon and Norman, 1963) This process gives rise to 1,4 (or $\gamma$)-diols

In the case of hydroxymethylation the $\alpha$-hydroxy-alkyl radical adds to the carbon atom of the carbonyl group of a free (nonsolvated) form of formaldehyde (the concentration of this form in alcohol increases with temperature exponentially (Silaev *et al*, 1979)) This process yields 1,2 (or $\alpha$)-diols

$\gamma$-Radiolysis of formaldehyde soluton in $C_1$–$C_3$ alcohols gives rise, along with 1,2-diols, to hydrogen and carbon oxide in low yields (exceeding, nevertheless, those of similar products in the radiolysis of the individual alcohols), and in $C_2$–$C_3$ alcohols (methanol homologues, i e ethanol 1- and 2-propanol) to methanol whose yields at elevated temperatures attain chain values, and also ethanediol (in low nonchain yields)† Also, it has been shown (Shadyro, 1975) that $\gamma$-radiolysis of formaldehyde solutions in $C_2$–$C_3$ alcohols gives rise to a simultaneous appearance, along with 1,2-diols, of carbonyl compounds (also in chain yields but one order of magnitude lower than those of 1,2-diols at the same temperatures and concentrations of the formaldehyde in the system). As this takes place the temperature dependences of the yields of the two products on formaldehyde concentration pass through a maximum and are symbate With increasing temperature
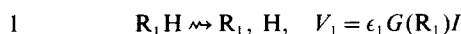
in the range between 303 and 473 K their yields in the $\gamma$-radiolysis of the solutions of formaldehyde (at its concentration in the bound and free forms of 1 M) in 1- and 2-propanol pass through a maximum whereas those of the carbonyl compounds and methanol only increase† The proposed (Shadyro, 1975) radiation hydroxymethylation mechanism for the saturated alcohols does not contain any competing reactions and it does not allow to describe the maximum on the experimental dependences of the 1,2-diol or carbonyl compound yields on formaldehyde concentration in the alcohol
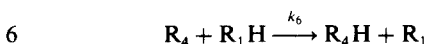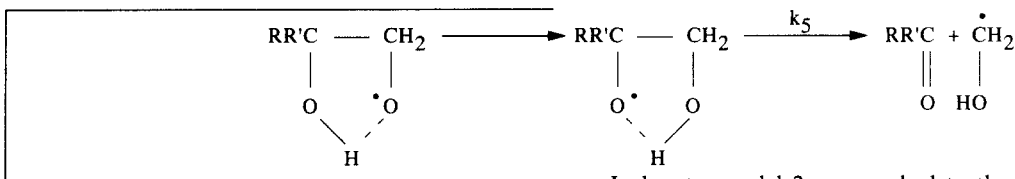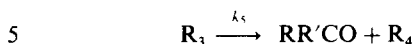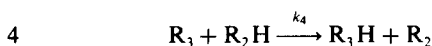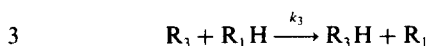
Analysis of the final products and comparison of their yields at various conditions permitted the development of kinetic models for radiation hydroxypropylation of alcohols (starting with methanol) and hydroxymethylation of their methanol homologues The processes consist of the following systems of the consecutive-parallel reactions

Model 1 for hydroxypropylation of alcohols starting with methanol (reactions 1–4, 7–9) and model 2 for hydroxymethylation of their methanol homologues (reactions 1–9)
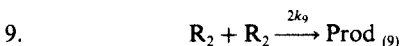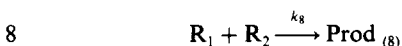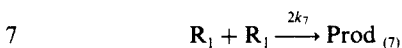
*I Chain initiation*

1                 $R_1H \rightsquigarrow R_1,\ H,\quad V_1 = \epsilon_1 G(R_1)I$

*II Chain propagation*

2                       $R_1 + R_2H \xrightarrow{k_2} R_1$

3                  $R_3 + R_1H \xrightarrow{k_3} R_3H + R_1$

4                  $R_3 + R_2H \xrightarrow{k_4} R_3H + R_2$

5                    $R_3 \xrightarrow{k_5} RR'CO + R_4$



6                  $R_4 + R_1H \xrightarrow{k_6} R_4H + R_1$

*III Chain termination*

7                    $R_1 + R_1 \xrightarrow{2k_7} \text{Prod}_{(7)}$

8                    $R_1 + R_2 \xrightarrow{k_8} \text{Prod}_{(8)}$

9.                   $R_2 + R_2 \xrightarrow{2k_9} \text{Prod}_{(9)}$

where $R_1H$ is the saturated alcohol of the type $RR'CHOH$ (R, R' is the hydrogen atom or alkyl), $R_2H$ is 2-propene-1-ol $CH_2{=}CHCH_2OH$ or the free form of formaldehyde $CH_2{=}O$, $R_3H$ is diol $RR'C$

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†The data are also due to A I Novoselov

$(OH)(CH_2)_nOH$ ($n = 3$ in model 1 and $n = 1$ in model 2), $RR'CO$ is the carbonyl compound, $R_4H$ is methanol $CH_3OH$, Prod is the final product of radicals recombination or disproportionation, $R_1$ is the $\alpha$-hydroxyalkyl radical $RR'COH$, any in model 1 or only with two and more carbon atoms in model 2, $R_2$ is the $\alpha$-hydroxypropenyl radical $CH_2{=}CHCHOH$ or formyl radical $H\dot{C}{=}O$, $R_3$ is the $\beta$-dihydroxyalkyl radical-adduct $RR'C(OH)CH_2$ $CHCH_2OH$ or hydroxyalkoxyl radical-adduct $RR'C(OH)CH_2O$, $R_4$ is the hydroxymethyl radical $\dot{C}H_2OH$, $V_1$ is the rate of reaction (1), $\epsilon_1$ is the electronic fraction of the saturated alcohol in the system, $G(R_1)$ is the radiation yield of the $\alpha$-hydroxyalkyl radicals including those that appear in the interaction of their precursors, i e alkoxyl radicals and hydrogen atoms, with the saturated alcohol (the solvated electrons react very slowly with the saturated alcohols (Pikaev and Kabakchi, 1982) and therefore are expected to be completely scavenged by the unsaturated component double bond in the system), $I$ is the dose rate

Model 1 contains two competing reactions (3) and (4) whereas model 2 contains three such reactions (3), (4) and (5) which may be responsible for a maximum appearing on the experimental dependences of the yields of 1,4- or 1,2-diol and carbonyl compound on 2-propene-1-ol or formaldehyde concentration in the system

In model 2 the mechanism of monomolecular reaction (5) consisting of the destruction of the radical-adduct $R_3$, includes, in all likelihood (Kalyazin et al, 1977), a stage of hydrogen atom transfer from the hydroxyl group to the adjacent terminal oxygen atom with an unpaired electron followed by the C–C bond breaking

In kinetic model 2, as supplied to the methanol-formaldehyde system (model 3) reaction (5) will represent a reverse stage of reaction (2) and is not discussed separately, radicals $R_1$ become identical to the hydroxymethyl radicals $R_4$, therefore reaction (6) is eliminated, and in reaction (7) the recombinations of the hydroxymethyl radicals (the disproportionation reaction for them can be ignored (Baxendale and Wardman, 1975, Seki et al, 1968)), will give ethanediol $R_3H$ as in reactions (3, 4)

7                       $R_1 + R_1 \xrightarrow{2k_7} R_3H$

## MATHEMATICAL ANALYSIS OF THE KINETIC MODELS

The mathematical analysis of the proposed kinetic models for the hydroxyalkylation processes consisted

of the compilation of a system of differential equations for changes in radical concentrations per unit time for each model, replacement of these equations by a system of algebraic equations with the use of a quasi-stationary concentrations technique and an analytical solution of such a model. In so doing, for those models in which three different pairs of two nonidentical radicals exist at the chain termination stage, the following conditions were used†.

$$k_8 = \sqrt{2k_7 2k_9}$$

and

$$V_1 = V_7 + 2V_8 + V_9 = (\sqrt{2k_7}\,[R_1] + \sqrt{2k_9}\,[R_2])^2$$

A next step was finding equations for the quasi-stationary radical concentration via concentrations of the stable substances and constants of the elementary stages with a subsequent substitution of the equations derived into those for the rate of the final product formation (considering that $G(\text{Prod.}) = V(\text{Prod})/I$, where $G$ is the radiation yield of the product, $V$ is the rate of its formation and $I$ is the dose rate). Finally, it was necessary to test whether the established function of the yield (formation rate) of the product (diol or carbonyl compound) satisfies the requisite condition for the existence of the extremum

$$\frac{\partial}{\partial x} G(\text{Prod.}) = \frac{\partial}{\partial x} V(\text{Prod})/I = 0$$

at parameters consistent with a physical meaning

The following analytical expressions for the radiation yields of the products were obtained

The functional expression (1) reaches an extremum at

$$k_2 = \left(\frac{\sqrt{\alpha l_m}}{x_m} + \frac{1}{\sqrt{\alpha l_m}}\right)^2 \sqrt{2k_7\epsilon_1 G(R_1)I} \qquad (2)$$

where $l_m$ and $x_m$ are the values of $l$ and $x$ at the extremum point.

On substituting $k_2$ by expression (2) in expression (1) we shall obtain a different form of the latter

$$G(R_3H)_{1,4} = \frac{\epsilon_1 G(R_1)x}{\dfrac{x^2}{\alpha l + x} + 1 \Big/ \left(\dfrac{\sqrt{\alpha l_m}}{x_m} + \dfrac{1}{\sqrt{\alpha l_m}}\right)^2} \qquad (3)$$

In the saturated alcohol (methanol homologue)–formaldehyde systems—model 2 (reactions 1–9):

$$G(R_3H)_{1,2} = \frac{\epsilon_1 G(R_1)k_2 x(\alpha l + x)}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_7 c_1 G(R_1)I}} \qquad (4)$$

$$G(RR'CO) = G(R_4H)$$
$$= \frac{\epsilon_1 G(R_1)k_2 x\beta}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_7 \epsilon_1 G(R_1)I}} \qquad (5)$$

where

$$\alpha = k_3/k_4, \quad \beta = k_5/k_4 \quad (\text{mol/dm}^3)$$

The ratio between the yields of 1,2-diol $R_3H$ and the carbonyl compound $RR'CO$ from expressions (4, 5) represent a simple linear function of $x$

$$\frac{G(R_3H)_{1,2}}{G(RR'CO)} = \frac{1}{\beta}x + \frac{\alpha}{\beta}l = \frac{k_4}{k_5}x + \frac{k_3}{k_5}l \qquad (6)$$

In the methanol–formaldehyde systems—model 3 (reactions 1–4, 7–9):

$$G(R_3H)_{ED} = \frac{\epsilon_1 G(R_1)(\alpha l + x)\{k_2 x[k_2 x^2 + (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}\,] + (\alpha l + x)2k_7\epsilon_1 G(R_1)I\}}{[k_2 x^2 + (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}\,]^2} \qquad (7)$$

In the systems saturated alcohol–2-propene-1-ol — model 1 (reactions 1–4, 7–9)

$$G(R_3H)_{1,4} = \frac{\epsilon_1 G(R_1)k_2 x(\alpha l + x)}{k_2 x^2 + (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}} \qquad (1)$$

where $\alpha = k_3/k_4$, $l$ is the concentration $[R_1H]$ of the saturated alcohol for a given initial concentration of $x$ of the unsaturated compound $[R_2H]$ Expression (1) is a function of one variable $x$ for condition of excess concentration of saturated alcohol in the system $[R_1H] \gg [R_2H]$ when any variation of its concentration $l$ may be neglected‡.

where $\alpha = k_3/k_4$.

If in the derivation of the analytical expression for the yield of ethanediol $R_3H$ in model 3 its formation by the recombination mechanism in reaction (7) is ignored as the product yield on this route represents an insignificant fraction of that on the main chain route in reaction (3), expression (7) converts to an expression for the yield of ethanediol $R_3H$, identical to expression (1).

If (1) $k_2 x^2 \ll (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}$, (2) $k_2 x^2 \simeq (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}$ (for the maximum) and (3) $k_2 x^2 \gg (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}$, expression (1) converts to the simple functions of the direct and inverse proportional relations according to conditions (1) and (3) respectively,

$$G(R_3H) = \frac{\epsilon_1 G(R_1)k_2 x}{\varphi\sqrt{2k_7\epsilon_1 G(R_1)I}} \qquad (8)$$

and

$$G(R_3H) = \frac{\epsilon_1 G(R_1)}{\varphi}\left(\frac{\alpha l}{x} + 1\right) \qquad (9)$$

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†In order to reduce the power of term $2k_7[R_1]^2$ in the equation $d[R_1]/dt = 0$ from 2 to 1 (see Section II of the Appendix)

‡More generally, passing from two variables $l$ and $x$ to a single variable, one must substitute initial concentrations of components in expression (1) by their corresponding mole fractions (Poluektov et al, 1974) $1 - x/(l + x)$ and $x/(l + x)$
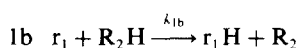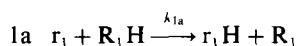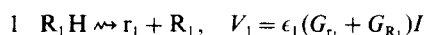
where $\varphi = 1$ for conditions (1, 3) and $\varphi = 2$ for condition (2) These relations describe the initial (on rising) and terminal (on lowering), respectively, portions of the kinetic dependences for the diol yield on unsaturated component concentration in the system Expression (4) for conditions (2) and (3) also converts to (9) and for condition (1)—to (8) only if $\alpha l \gg \beta$ For conditions (2) and (3) expression (5) converts similarly to an expression for an inverse-proportional relation

$$G(RR'CO) = \frac{\epsilon_1 G(R_1)\beta}{\varphi x} \quad (10)$$

One-parameter expressions (8–10) allow to roughly estimate the parameters $k_2$, $\alpha$ and $\beta$ from the experimental product yields and values of $2k_7$ and $G(R_1)$

Let us consider how some of the alternative models of the saturated alcohol hydroxyalkylation processes

In this context, instead of models 1 and 2 one can use the corresponding models 4 and 5 in which reaction (4) competing with reaction (3) in models 1 and 2 and reaction (5) in model 2 at the chain propagation stage are replaced by two additional competing reactions (1a, 1b) involving hydrogen atoms or alkoxyl radicals from the saturated alcohol, appearing at the first radiolysis stage in reaction (1)

1   $R_1H \rightsquigarrow r_1 + R_1, \quad V_1 = \epsilon_1(G_{r_1} + G_{R_1})I$

1a   $r_1 + R_1H \xrightarrow{k_{1a}} r_1H + R_1$

1b   $r_1 + R_2H \xrightarrow{k_{1b}} r_1H + R_2$

(or the addition reaction to give $r_2$)

where $r_1$ is the hydrogen atom or alkoxyl radical, $r_2$ is the radical-adduct, $G_{r_1}$ is the total initial yield of hydrogen atoms and alkoxyl radicals upon completion of the reaction in the spurs, $G_{R_1}$ is the initial yield of the $\alpha$-hydroxy- alkyl radicals $R_1$, i e with no consideration for their appearance in the secondary radiolysis processes by reaction (1a)

In models 4 and 5 the functions of the diol $R_3H$ yield

$$G(R_3H)_{1,4} = \frac{\epsilon_1[(G_{r_1} + G_{R_1})\gamma l + G_{R_1}x]k_2 x}{(\gamma l + x)\sqrt{2k_7\epsilon_1(G_{r_1} + G_{R_1})I}} \quad (11)$$

and

$$G(R_3H)_{1,2} = \frac{\epsilon_1[(G_{r_1} + G_{R_1})\gamma l + G_{R_1}x]k_2 k_3 lx}{(k_3 l + k_5)(\gamma l + x)\sqrt{2k_7\epsilon_1(G_{r_1} + G_{R_1})I}} \quad (12)$$

respectively, where $\gamma = k_{1a}/k_{1b}$ reach an extremum at the common values of the parameters with no physical meaning

$$x_m = \gamma l_m(\sqrt{-G_{r_1}/G_{R_1}} - 1) \quad (13)$$

i e at $G_{r_1} < 0$ or $G_{R_1} < 0$ Hence, competing reactions (1a, 1b) in models 4 and 5 cannot be responsible of the appearance of a maximum on the experimental dependence Instead, this role is played by competing reaction (3, 4) in models 1 and 2 This allows to discriminate models 4 and 5 in favour of the corresponding models 1 and 2

Analysis of the other models with the only difference from models 1 and 2 in that their chain terminates due to the following radical destruction reactions $R_2 + R_2$ (models 6, 9), $R_2 + R_1$ (models 7, 10) or $R_2 + R_3$ (models 8, 11), indicates that the expression for the diol $R_3H$ yield in these models is the same and identical to the inverse-proportional relation function (9), i e without any extremum Hence, models 6–8 and 9–11 can be equally discriminated in favour of models 1 and 2

One more alternative for model 2 can be represented by model 12 which assumes the abstraction of the hydrogen atom with the radical-adduct $R_3$ in reaction (4) not from the free but rather the bound form of the formaldehyde $RO(CH_2O)_nH$, where $n = 1–4$ (Glushonok et al, 1983), whose concentration in the alcohol is far higher than that of the free one In model 12 the expression for the 1,2-diol $R_3H$ yield is as follows

$$G(R_3H)_{12} = \frac{\epsilon_1 G(R_1)k_2 x(\alpha l + z)}{k_2 xz + (\alpha l + \beta + z)\sqrt{2k_7\epsilon_1 G(R_1)I}} \quad (14)$$

where $z = ([RO(CH_2O)_nH] - [CH_2O])$ is the difference between the concentrations of the free and bound formaldehyde forms in the alcohol Later on it will be shown that model 12 cannot describe the maximum on the experimental kinetic dependence

Note that the analytical expressions for the product yields in the course of radiation hydroxyalkylation can be also used for describing the functional dependences of the yields in similar peroxide-initiated processes provided that the radiation yields $G(Prod)$ and $\epsilon_1 G(R_1)$ in these expressions are replaced by the corresponding product formation and initiation rates

## RECONSTRUCTION OF FUNCTIONAL DEPENDENCES FROM THE EMPIRICAL DATA

Tentative estimates of the parameters $G(R_1)$, $k_2$, $\alpha$ and $\beta$ from the analytical expressions for the product yields in the hydroxyalkylation processes were made as follows

Constants $2k_7$ for the rate of the $\alpha$-hydroxyalkyl-radical destruction in the saturated individual alcohols at 298 K, involved in these expressions, are given elsewhere (Silaev et al, 1986b) These values were extrapolated to the experimental temperatures by the Arrhenius equation with the use of effective self-diffusion energies of the corresponding alcohols (Silaev et al, 1986b)

The $G(R_1)$ values (see Table 1) were found by extrapolating the total yield of the α-hydroxyalkyl (Feldman et al, 1984), alkoxyl radicals (Belevsky, 1981) and hydrogen atoms (Pikaev, 1986) in the individual alcohols (according to the mechanism adopted) by the Arrhenius equation (Silaev et al, 1986b) to the temperatures of the process, known from the ESR data at 298 K In so doing, use was made of the experimentally obtained effective activation energies for the formation of vicinal diols resulting from the recombination of the α-hydroxyalkyl radicals in the temperature region for alcohol γ-radiolysis up to the onset of the radiation-thermal destruction (Silaev, 1989). The activation energy for the hydrogen yields in the saturated alcohols $C_1$–$C_3$ was taken to be zero by analogy with practically the same value for the yields of the solvated electrons escaping the decay in the spurs (Dixon et al, 1975, 1976, Jha and Freeman, 1968)

The values of $k_2$, α and β were found by an algebraic technique from expressions (8–10) including any of these parameters by substituting the values of $2k_7$, $G(R_1)$ and the experimental product yields, obtained by the above method, into these expressions An arithmetic average from the totality of the values of a given parameter for each experimental point on the dependence of the product yield on unsaturated component concentration in the system was used as its tentative estimate

The nonlinear estimation of the model parameters (Bard, 1979) was performed by using a least-squares technique In so doing, one had to take such values of the unknown parameters which gave the smallest sum of squares deviation from the experimental dependence to minimize the functional composed on the basis of one of the analytical expressions found for the radiation yields The minimization procedure was performed as proposed by Rosenbrook (Himmelblau, 1975) (FORTRAN) with the use of a standard library MNB1R sub-program as applied to a specific analytical expression The tentative estimates of the parameters were used as the initially set values for minimization purposes (see Table 1).

The functional dependence of the yields of 1,4-diols on the initial concentration of 2-propene-1-ol in the saturated $C_1$–$C_3$ alcohols–2-propene-1-ol systems at 433 K, corresponding to model 1, was reconstructed from the empirical data (Silaev, 1990) with the aid of expression (3) (see Fig 1) It allowed to minimize the appropriate functional both by three and two parameters, $G(R_1)$, α, $x_m$ and $G(R_1)$, α, respectively In the latter case used as the known parameter was the maximum value of $x_m$ found from the

Table 1 Parameters estimated† by analytical expressions for the radiation yields of diols in the systems composed of unsaturated alcohol and 2-propene-1-ol or formaldehyde at various temperatures

| System | $k_2^a$ $\left(\dfrac{dm^3}{mol\ s}\right)$ | $k_2^b$ $\left(\dfrac{dm^3}{mol\ s}\right)$ | $\alpha^a$ | $\alpha^b$ | $\beta^a$ $\left(\dfrac{mol}{dm^3}\right)$ | $\beta^b$ $\left(\dfrac{mol}{dm^3}\right)$ | $x_m^a$ $\left(\dfrac{mol}{dm^3}\right)$ | $G(R_1)^a$ $\left(\dfrac{molec}{100\ eV}\right)$ | $G(R_1)^d$ $\left(\dfrac{molec}{100\ eV}\right)$ | $S_{Y(a)}^f$ | $S_{Y(b)}^f$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 Methanol-2-propene-1-ol (433 K)‡ | 2 5 10⁴ | 1 6 10⁴ | 1 2 10⁻² | 4 0 10⁻³ | | | 3 8 10⁻² | 3 6 | 7 6 | 5 7 10⁻¹ | 2 8 |
| 2 Ethanol-2-propene-1-ol (433 K)‡ | 6 5 10⁴ | 5 9 10⁴ | 2 7 10⁻² | 2 6 10⁻² | | | 3 7 10⁻² | ¹0 1 | 10 3 | 7 8 10⁻¹ | 2 0 |
| 3 1-Propanol-2-propene-1-ol (433 K)‡ | 2 7 10⁴ | 3 1 10⁴ | 2 4 10⁻² | 4 4 10⁻² | | | 4 1 10⁻² | 9 3 | 6 7 | 6 9 10⁻¹ | 2 7 |
| 4 2-Propanol-2-propene-1-ol (433 K)‡ | 1 0 10⁵ | 1 1 10⁵ | 6 8 10⁻² | 1 0 10⁻¹ | | | 3 9 10⁻² | 10 1 | 7 3 | 1 9 | 2 3 |
| 5 Ethanol-formaldehyde (413 K)§ | 1 5 10⁴ᶜ | 1 6 10⁴ | 1 2 10⁻¹ | 9 4 10⁻² | 1 6 10⁻¹ | 1 4 10⁻¹ | | 9 4ᵉ | 9 8 | 10 7 | 12 3 |
| 6 Ethanol-formaldehyde (443 K)§ | 2 1 10⁴ᶜ | 1 5 10⁴ | 6 5 10⁻² | 6 0 10⁻² | 8 5 10⁻² | 9 0 10⁻² | | 10 5ᵉ | 10 6 | 7 4 | 10 2 |
| 7 1-Propanol-formaldehyde (413 K)§ | 6 0 10³ | 5 5 10³ | 3 6 10⁻¹ | 3 0 10⁻¹ | 2 5 10⁻¹ | 2 0 10⁻¹ | | 9 0ᵉ | 6 5 | 4 7 | 11 9 |

†Relative error in the estimates of the model 1 parameters (systems 1–4) < 15%, model 2 (systems 5–7) < 25% ‡See Silaev (1990) §See Shadyro (1975)

aEstimates obtained by nonlinear minimization with three parameters of the functional composed by the analytical expression for the diol yield

bAverage parameter estimate obtained algebraically from one-parameter expressions (8–10) using constants $2k_7$ (Silaev et al, 1986b) and the yields $G(R_1)^d$ as determined from the ESR data

cThe estimated constants $k_2$ for the addition of the α-hydroxyethyl radicals to the formaldehyde at 413 and 443 K gave a rough estimate of $Ea_{eff}$ = 16 7 ± 5 kJ/mol

dYield of the α-hydroxyalkyl radicals $R_1$, calculated from the ESR data at 293 K as a total yield of the hydrogen atoms at 293 K (Pikaev, 1986) and those of the hydroalkyl (Feldman et al, 1984) and alkoxyl (Belevsky, 1981) radicals, extrapolated to the experimental temperatures

eEstimated yield of the α-hydroxyalkyl radicals $R_1$, obtained by minimization with three parameters of the functional composed by analytical expression (3) in model 1 and extrapolated from the temperatures of hydroxypropylation to those of hydroxymethylation

f$S_{Y(a)}$ and $S_{Y(b)}$ are the standard deviations in the approximations of the functions containing parameters which were estimated by (a) minimization of the functionals and (b) expressions (8–10), respectively
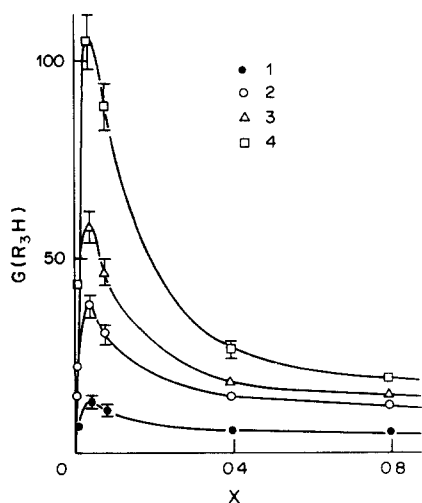
Fig 1 Results of the restoration of the functional dependence of the yields $G(R_3H)$ (molec /100 eV) of 1,4-butanediol (1), 1,4-hexanediol (2), 1,4-pentanediol (3) and 2-methyl-2,5-pentanediol (4) on the initial concentration $x$ (mol/dm³) of 2-propene-1-ol (calculated curves) in methanol (1), 1-propanol (2), ethanol (3) and 2-propanol (4), respectively, at 433 K from the corresponding experimental data–points (Silaev, 1990)



Fig 2 Results of the restoration of the functional dependence of the yields $G(R_3H)$ (molec /100 eV) of 1,2-propanediol (1, 2) and 1,2-butanediol (3) on the initial concentration $x$ (mol/dm³) of the free form of the formaldehyde (calculated curves) in ethanol at 413 K (1), 433 K (2) and 1-propanol at 413 K (3) from the experimental data–points (Shadyro, 1975)

experimental dependence plot, equal to 0 04 M for all four alcohol systems at 433 K As opposed to $x_m$, the $l_m$ value in expression (3) can be determined rather accurately since when $x_m$ around 0 04 M varies by 50%, $l_m$ variation does not exceed 0 3% The $G(R_1)$, $\alpha$ and $x_m$ estimates obtained by minimization with the three parameters for the four alcohol systems as well as the $k_2$ values calculated from them by expression (2) and standard deviation $S_Y$ of the functions approximation are given in Table 1 As compared with the results obtained by the functional minimization using three parameters, the same procedure with two parameters $G(R_1)$ and $\alpha$, at $x_m = 0\,04$ M, results in the derivations of the $G(R_1)$ and $\alpha$ estimates not exceeding 12%

When the empirical data (Shadyro, 1975) (see Figs 2 and 3) were taken to restore the functional dependence of the product yields on the initial concentration of the free (nonsolvated) form of formaldehyde in the saturated alcohol–formaldehyde systems, complying with model 2, use was made of the 1,2-diol yields only The fact is that they are more reliable as compared with those of the carbonyl compounds capable of reacting with the alcohol Note that such an interaction depends heavily on the temperature and acidity of the medium (Walker, 1964) The functional expression (4) for the 1,2-diol yield contains four unknown parameters, viz $G(R_1)$, $k_2$, $\alpha$ and $\beta$. Generally, such unimodal curves can be adequately described in mathematical terms with the aid of a three-parameter parabolic function Therefore in the presence of a limited number of experimental points (see Figs 2 and 3) the problem was to avoid a sharp growth of the random error in determining the parameters and their excessive mutual
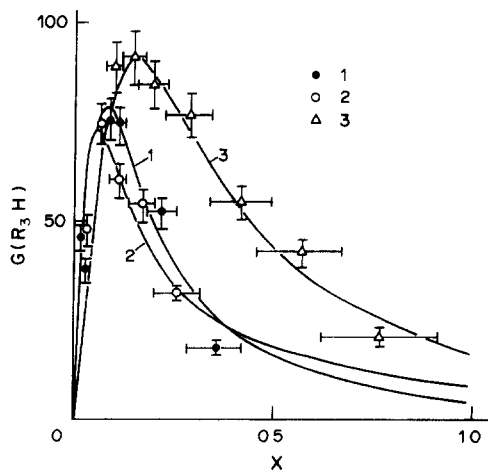
correlation (Bard, 1979) Then, to reduce the number of parameters in the minimization procedure with the use of expression (4) in model 2 the yields $G(R_1)$ in the saturated alcohol–formaldehyde systems were replaced, in view of the identical hydroxyalkylation kinetics, by estimates of the same yields in the saturated alcohol–2-propene-1-ol systems with a matching alcohol as the solvent The yields were obtained by minimizing the functional for these systems composed by expression (3) in model 1 and extrapolated (by the above technique) from the temperature of hydroxypropylation to those of hydroxymethylation (see Table 1) The concentration $x$ of the free form of the formaldehyde from its total concentration in the system, involved in
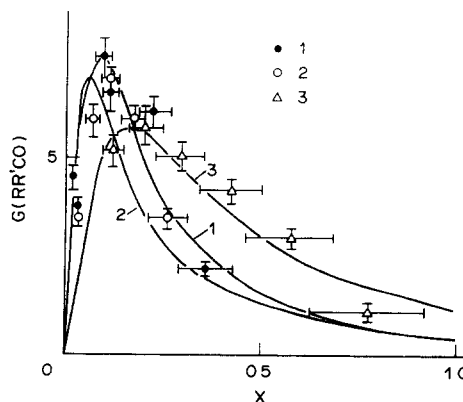


Fig 3 Results of the restoration of the functional dependence $G(RR'CO)$ (molec /100 eV) of acetaldehyde (1, 2) and propionic aldehyde (3) on the initial concentration $x$ (mol/dm³) of the free form of the formaldehyde (calculated curves) in ethanol at 413 K (1), 443 K (2) and 1-propanol at 413 K (3) from the experimental data–points (Shadyro, 1975) Standard deviations (1) $-$ 1 3, (2) $-$ 1 7, (3) $-$ 0 5

expressions (4, 5), was calculated by empirical formulae given elsewhere (Silaev et al, 1979) and valid for the temperature interval between 343 and 435 K with relative error less than 20% for the given alcohols and conditions.

The estimated parameters and standard deviations $S_Y$ obtained in the minimization of the functional composed by expression (4) using three parameters $k_2$, $\alpha$ and $\beta$ are presented in Table 1 Figure 3 shows the restoration of the functional dependence by expression (5) from the experimental data for the yields of the carbonyl compounds using estimated parameters that follow from minimizing a functional composed by expression (4) for the experimental yields of 1,2-diols Figures 1–3 demonstrate the degree of the mathematical adequacy in describing the experimental dependences and suggest a sufficient suitability of models 1 and 2 for the real hydroxyalkylation processes

Using expression (14) in model 12 with three unknown parameters $k_2$, $\alpha$ and $\beta$ in the restoration of the functional dependence from the empirical data indicates that this model does not describe the maximum on the experimental curves and therefore can be discriminated in favour of model 2.

The obtained sequence in the estimated values of $k_2$ for the reaction rates in the addition of the $\alpha$-hydroxyalkyl radicals to the unsaturated compounds in the systems composed of methanol, 1-propanol, ethanol and 2-propanol correlates with that made up of such macroscopic properties of the saturated alcohols as hydrogen bonding entropy, energy corresponding to the wavelength in the maximum of the optical absorption of the solvated electrons, and effective energy of self-diffusion activation (Silaev et al, 1990)

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# APPENDIX

## *I Models 1 and 2 do not Contain the Reactions Below*

(a) A primary act of the radiation–unsaturated compound interaction

$$1a \quad R_2H \rightsquigarrow R_2, H$$

since the electronic fraction $\epsilon_2$ of the unsaturated component $R_2H$ is far lower than the electronic fraction $\epsilon_1$ of the solvent, i e saturated alcohol $R_1H$ ($\epsilon_2 \ll \epsilon_1$)

(b) A reaction parallel to reaction (2)

$$2a \quad R_1 + R_2H \xrightarrow{k_{2a}} R_1H + R_2$$
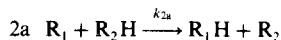
since reaction (2a), contrary to addition reaction (2), plays no critical role in chain propagation and is not essential for describing the process The rates ratio $V_2/V_{2a} = k_2/k_{2a}$ is independent of unsaturated compound concentration in the system

(c) An addition reaction parallel to reaction (4)

$$4a \quad R_3 + nR_2H \xrightarrow{k_{4a}} R_3(R_2H)_n^{\bullet}$$
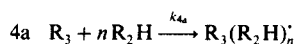
where $n \geqslant 1$ since model 1 suggests that the radical-adducts $R_3$ with a free valence at the $\beta$-carbon atom are insufficiently reactive (possibly due to steric hindrances induced by the —$CH_2OH$ group) to be added at the double bond in reaction (4a) at a rate comparable to that of both reaction (4) and reaction (3), i e $V_{4a} \ll V_4$ and $V_{4a} \ll V_3$ Then, in model 2 the addition of the hydroxyalkoxyl radical-adducts $R_3$ to the formaldehyde $R_2H$ at elevated temperatures is very improvable as no ether bond-containing compounds have been reported elsewhere (Dolmatov and Polak, 1965)
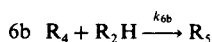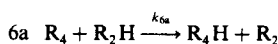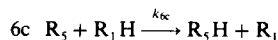
(d) An addition reaction

$$4b \quad R_2 + nR_2H \xrightarrow{k_{4b}} R_2(R_2H)_n^{\bullet}$$
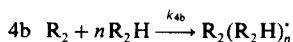
where $n \geqslant 1$ since in model 1 this reaction, as is known from the field of 2-propene-1-ol polymerization (Dolmatov and Polak, 1963, 1965), is low-effective and not essential for describing the process of 1,4-diol formation Moreover, in model 2 the reaction by which the formyl radicals $R_2$ add to the formaldehyde $R_2H$ whose increase in the system brings about a chain-type formation of glycol aldehyde cannot be effective either, because otherwise a chain process in the formation of this product would develop, which is not the case

(e) Reactions (1, 3, 4) in model 1 and (1, 3, 4, 6) in model 2 with the abstraction of the hydrogen atoms in the $C_2$–$C_3$ alcohols not from the $\alpha$-position to give $\beta$- (and, in the case of 1-propanol, $\gamma$-) hydroxyalkyl radicals These radicals are expected to yield diols, without chain termination, with a greater distance between the hydroxyl groups (and higher boiling temperatures) However, such diols have not been chromatographically detected in significant yields with respect to the main diol type

(f) In addition, model 2 does not include the feasible reactions of the hydroxymethyl radicals $R_4$ with the formaldehyde $R_2H$, leading to a side process by which 1,2-diol is formed containing fewer carbons than in the parent alcohol, i e ethanediol $R_5H$

$$6a \quad R_4 + R_2H \xrightarrow{k_{6a}} R_4H + R_2$$

$$6b \quad R_4 + R_2H \xrightarrow{k_{6b}} R_5$$

and then

$$6c \quad R_5 + R_1H \xrightarrow{k_{6c}} R_5H + R_1$$

since, first, reaction (6a), as compared with addition reaction (6b), can be ignored for the same reason as the above reaction (2a) with respect to reaction (2) and, second, the chain initiation of methanol and the absence of such a process for ethanediol in the radiolysis of the nonmethanol alcohol-formaldehyde systems suggests that the hydroxymethyl radicals $R_4$ appearing from reaction (5) undergo a fast interaction by reaction (6) with the adjacent molecules of the alcohol (solvent) $R_1H$, including that from the solvation shell of the radical In this case they do not have time to diffuse in the solution for a distance required to come across the molecules of the formaldehyde $R_2H$ so that the feasible reactions (6a–6c) will be insignificant for the kinetics of the process as a whole (small amounts of ethanediol may appear in the nonmethanol alcohol-formaldehyde systems as a result of the recombination of a small fraction of the hydroxymethyl radicals $R_4$)

Note that if model 2 includes reaction (6b, 6c) to become model 2a, expressions (4, 5) will remain unaltered

## *II The Derivations of the Analytical Expressions for the Yields (Formation Rates) of the Final Products in Models 1, 2 and 3*

The following conditions and conventional signs were used

$$k_8 = \sqrt{2k_7 2k_9},$$

$$\sqrt{V_1} = \sqrt{V_7 + 2V_8 + V_9} = (\sqrt{2k_7}\,[R_1] + \sqrt{2k_9}\,[R_2])$$

and

$$\sqrt{2k_7 V_1} = \sqrt{2k_7\epsilon_1 G(R_1)}I = \delta_1,$$

$$k_3/k_4 = \alpha, \quad k_5/k_4 = \beta,$$

$$[R_1H] = l, \quad [R_2H] = \lambda$$

(a) The derivation of the expression (1) of model 1 (reactions 1–4, 7–9)

$$V(R_1H)_{1 4} = V_3 + V_4 = V_2 = (k_3 l + k_4 x)[R_3] = k_2 x[R_1]$$

$$d[R_3]/dt = V_2 - V_3 - V_4$$

$$= k_2 x[R_1] - (k_3 l + k_4 x)[R_3] = 0$$

$$[R_3] = \frac{k_2 x[R_1]}{(k_3 l + k_4 x)}$$

$$d[R_1]/dt = V_1 + V_3 - V_2 - V_7 - V_8$$

$$= V_1 + k_3 l[R_3] - k_2 x[R_1]$$

$$\quad - 2k_7\,[R_1]^2 - \sqrt{2k_7 2k_9}\,[R_1][R_2]$$

$$= V_1 + k_3 l[R_3] - k_2 x[R_1]$$

$$\quad - \sqrt{2k_7}\,(\sqrt{2k_7}\,[R_1] + \sqrt{2k_9}\,[R_2])[R_1]$$

$$= V_1 + k_3 l[R_3] - k_2 x[R_1] - \sqrt{2k_7 V_1}\,[R_1]$$

$$= V_1 + \frac{k_2 k_3 lx[R_1]}{(k_3 l + k_4 x)} - k_2 x[R_1] - \delta_1[R_1]$$

$$= V_1 + \frac{k_2 \alpha lx[R_1]}{(\alpha l + x)} - (k_2 x + \delta_1)[R_1] = 0$$

$$d[R_1]/dt = V_1(\alpha l + x)$$

$$= k_2 \alpha l x[R_1] - (k_2 x + \delta_1)(\alpha l + x)[R_1]$$

$$= V_1(\alpha l + x) - [(k_2 x + \delta_1)(\alpha l + x) - k_2 \alpha l x][R_1]$$

$$= V_1(\alpha l + x) - [k_2 x^2 + (\alpha l + x)\delta_1][R_1] = 0$$

$$[R_1] = \frac{V_1(\alpha l + x)}{k_2 x^2 + (\alpha l + x)\delta_1}$$

$$G(R_3H)_{1,4} = V(R_3H)_{1,4}/I = k_2 x[R_1]/I$$

$$= \frac{\epsilon_1 G(R_1)k_2 x(\alpha l + x)}{k_2 x^2 + (\alpha l + x)\sqrt{2k_7 \epsilon_1 G(R_1)I}} \qquad (1)$$

(b) The derivation of the expression (2) of model 1 (reactions 1–4, 7–9)

$$G(R_3H)_{1,4} = \frac{\epsilon_1 G(R_1)k_2 x(\alpha l + x)}{k_2 x^2 + (\alpha l + x)\sqrt{2k_7 \epsilon_1 G(R_1)I}}$$

$$= \frac{Ax^2 + Bx}{Cx^2 + Dx + E}$$

where

$$A = \epsilon_1 G(R_1)k_2, \quad B = \epsilon_1 G(R_1)k_2 \alpha l, \quad C = k_2,$$

$$D = \sqrt{2k_7 \epsilon_1 G(R_1)I} = \delta_1,$$

$$E = \alpha l \sqrt{2k_7 \epsilon_1 G(R_1)I} = \alpha l \delta_1$$

$$\partial G(R_3H)_{1,4}/\partial x = (2Ax + B)(Cx^2 + Dx + E)$$

$$- (Ax^2 + Bx)(2Cx + D)$$

$$= (AD - BC)x^2 + 2AEx + BE = 0$$

$$\tfrac{1}{2}(BC - AD)x^2 - AEx - \tfrac{1}{2}BE = 0$$

$$x_m = \frac{AE + \sqrt{A^2 E^2 + (BC - AD)BE}}{BC - AD}$$

$$= \frac{G(R_1)k_2 \alpha l_m \delta_1 + G(R_1)k_2 \alpha l_m \sqrt{k_2 \alpha l_m \delta_1}}{G(R_1)k_2^2 \alpha l_m - G(R_1)k_2 \delta_1}$$

$$= \frac{G(R_1)k_2 \alpha l_m (\delta_1 + \sqrt{k_2 \alpha l_m \delta_1})}{G(R_1)k_2 (k_2 \alpha l_m - \delta_1)}$$

$$= \frac{\alpha l_m \sqrt{\delta_1}(\sqrt{k_2 \alpha l_m} + \sqrt{\delta_1})}{(\sqrt{k_2 \alpha l_m} - \sqrt{\delta_1})(\sqrt{k_2 \alpha l_m} + \sqrt{\delta_1})}$$

$$= \frac{\alpha l_m \sqrt{\delta_1}}{(\sqrt{k_2 \alpha l_m} - \sqrt{\delta_1})}$$

$$k_2 = \left(\frac{\sqrt{\alpha l_m}}{x_m} + \frac{1}{\sqrt{\alpha l_m}}\right)^2 \delta_1 \qquad (2)$$

(c) The derivation of the expressions (4) and (5) of model 2 (reactions 1–9)

$$V(R_3H)_{1,2} = V_3 + V_4 = (k_3 l + k_4 x)[R_3]$$

$$V(RR'CO) = V_5 = V_6 = k_5[R_3] = k_6 l[R_4] = V(R_4H)$$

$$d[R_4]/dt = V_5 - V_6 = k_5[R_3] - k_6 l[R_4] = 0$$

$$[R_4] = \frac{k_5[R_3]}{k_6 l}$$

$$d[R_3]/dt = V_2 - V_3 - V_4 - V_5$$

$$= k_2 x[R_1] - (k_3 l + k_4 x + k_5)[R_3] = 0$$

$$[R_3] = \frac{k_2 x[R_1]}{(k_3 l + k_5 + k_4 x)}$$

$$d[R_1]/dt = V_1 - V_2 + V_3 + V_6 - V_7 - V_8$$

$$= V_1 - k_2 x[R_1] + k_3 l[R_3] + k_6 l[R_4]$$

$$- 2k_7[R_1]^2 - \sqrt{2k_7 2k_9}\,[R_1][R_2]$$

$$= V_1 - k_2 x[R_1] + k_3 l[R_3] + \frac{k_5 k_6 l[R_3]}{k_6 l}$$

$$- \sqrt{2k_7}\,(\sqrt{2k_7}[R_1] + \sqrt{2k_9}\,[R_2])[R_1]$$

$$= V_1 - k_2 x[R_1] + \frac{k_2 k_3 lx[R_1]}{(k_3 l + k_5 + k_4 x)}$$

$$+ \frac{k_2 k_5 x[R_1]}{(k_3 l + k_5 + k_4 x)} - \sqrt{2k_7 V_1}\,[R_1]$$

$$= V_1 - k_2 x[R_1] + \frac{k_2 \alpha l x[R_1]}{(\alpha l + \beta + x)}$$

$$+ \frac{k_2 \beta x[R_1]}{(\alpha l + \beta + x)} - \delta_1[R_1] = 0$$

$$d[R_1]/dt = V_1(\alpha l + \beta + x) - [k_2 x(\alpha l + \beta + x)$$

$$- k_2 \alpha l x - k_2 \beta x + (\alpha l + \beta + x)\delta_1][R_1]$$

$$= V_1(\alpha l + \beta + x)$$

$$- [k_2 x^2 + (\alpha l + \beta + x)\delta_1][R_1] = 0$$

$$[R_1] = \frac{V_1(\alpha l + \beta + x)}{k_2 x^2 + (\alpha l + \beta + x)\delta_1}$$

$$G(R_3H)_{1,2} = V(R_3H)_{1,2}/I = (k_3 l + k_4 x)[R_3]/I$$

$$= \frac{k_2 x(k_3 l + k_4 x)[R_1]}{(k_3 l + k_5 + k_4 x)I} = \frac{k_2 x(\alpha l + x)[R_1]}{(\alpha l + \beta + x)I}$$

$$= \frac{\epsilon_1 G(R_1)k_2 x(\alpha l + x)}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_7 \epsilon_1 G(R_1)I}} \qquad (4)$$

$$G(RR'CO) = G(R_4H) = V(RR'CO)/I$$

$$= V(R_4H)/I = k_5[R_3]/I$$

$$= \frac{k_2 k_5 x[R_1]}{(k_3 l + k_5 + k_4 x)I} = \frac{k_2 x\beta[R_1]}{(\alpha l + \beta + x)I}$$

$$= \frac{\epsilon_1 G(R_1)k_2 x\beta}{k_2 x^2 + (\alpha l + \beta + x)\sqrt{2k_7 \epsilon_1 G(R_1)I}} \qquad (5)$$

(d) The derivation of the expression (7) of model 3 (reactions 1–4, 7–9)

$$V(R_3H)_{ED} = V_3 + V_4 + V_7$$

$$= (k_3 l + k_4 x)[R_3] + 2k_7[R_1]^2$$

$$d[R_3]/dt = V_2 - V_3 - V_4$$

$$= k_2 x[R_1] - (k_3 l + k_4 x)[R_3] = 0$$

$$[R_3] = \frac{k_2 x[R_1]}{(k_3 l + k_4 x)}$$

$$d[R_1]/dt = V_1 - V_2 + V_3 - V_7 - V_8$$

$$= V_1 - k_2 x[R_1] + k_3 l[R_3] - 2k_7[R_1]^2$$

$$- \sqrt{2k_7 2k_9}\,[R_1][R_2]$$

$$= V_1 - k_2 x[R_1] + k_3 l[R_3]$$

$$- \sqrt{2k_7}\,(\sqrt{2k_7}\,[R_1] + \sqrt{2k_9}\,[R_2])[R_1]$$

$$= V_1 - k_2 x[R_1] + \frac{k_2 k_3 lx[R_1]}{(k_3 l + k_4 x)} - \sqrt{2k_7 V_1}[R_1]$$

$$= V_1 - \left[k_2 x - \frac{k_2 \alpha l x}{(\alpha l + x)} + \delta_1\right][R_1]$$

$$= V_1 - \frac{[k_2 x(\alpha l + x) - k_2 \alpha l x + (\alpha l + x)\delta_1][R_1]}{(\alpha l + x)}$$

$$= V_1 - \frac{[k_2 x^2 + (\alpha l + x)\delta_1][R_1]}{(\alpha l + x)} = 0$$

$$d[R_1]/dt = V_1(\alpha l + x) - [k_2 x^2 + (\alpha l + x)\delta_1][R_1] = 0$$

$$[R_1] = \frac{V_1(\alpha l + x)}{k_2 x^2 + (\alpha l + x)\delta_1}$$

$$G(R_3H)_{ED} = V(R_3H)_{ED}/I = \frac{k_2 x(k_3 l + k_4 x)[R_1]}{(k_3 l + k_4 x)I} + \frac{2k_7[R_1]^2}{I} = \frac{[R_1]}{I}(k_2 x + 2k_7[R_1])$$

$$= \frac{V_1(\alpha l + x)}{[k_2 x^2 + (\alpha l + x)\delta_1]I}\left\{k_2 x + \frac{2k_7 V_1(\alpha l + x)}{[k_2 x^2 + (\alpha l + x)\delta_1]}\right\}$$

$$= \frac{\epsilon_1 G(R_1)(\alpha l + x)\{k_2 x[k_2 x^2 + (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}\,] + (\alpha l + x)2k_7\epsilon_1 G(R_1)I\}}{[k_2 x^2 + (\alpha l + x)\sqrt{2k_7\epsilon_1 G(R_1)I}\,]^2} \tag{7}$$

## REFERENCES TO APPENDIX

Dolmatov S A and Polak L S (1963) Radiation polymerization of allyl alcohol and some of its derivatives *Neftekhimiya* **3**, 683

Dolmatov S A and Polak L S (1965) Kinetics of radiation induced allyl polymerization I *Kinetika i Kataliz* **6**, 797