

## Formaldehyde Solutions

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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 concentrations 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. The experimental dependence of the ethanediol radiation-chemical yields on formaldehyde concentration in  $\gamma$ -radiolysis of methanol–formaldehyde system at 373–473 K is shown.

**Keywords :** Nonbranched-Chain Process, Free Formaldehyde, 1-Hydroxyalkyl Radical, Formyl Radical, Competing Reaction, Equation

### I. 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<sup>-1</sup> (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 near-est-neighbor molecules of the solvent or unsolvated formaldehyde and, due to its structure, decompose by a monomolecular mechanism including isomerization [7, 8].

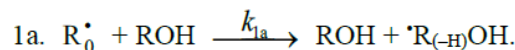
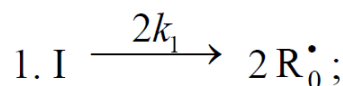
The analysis of stable liquid-phase products was carried out by the gas chromatographic method. The quasi-steady-state treatment is used to obtain kinetic equations.

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

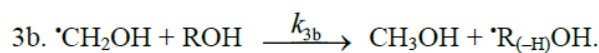
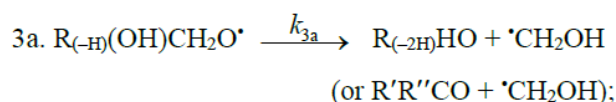
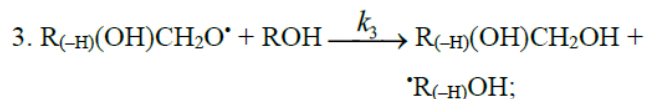
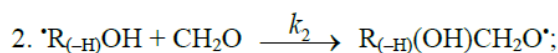
Free 1-hydroxyalkyl radicals (which result from the abstraction of a hydrogen atom from the carbon atom bonded to the hydroxyl group in molecules of saturated aliphatic alcohols but methanol under the action of chemical initiators [9, 10], light [11, 12], or ionizing radiation [13, 14]) add at the double 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  $\gamma$ -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<sup>-3</sup>, the dependence of the 1,2-alkanediol 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  $\gamma$ -radiolysis of individual alcohols) [7, 14, 15]. The available experimental data can be described in terms of the following scheme of reactions.

#### Scheme

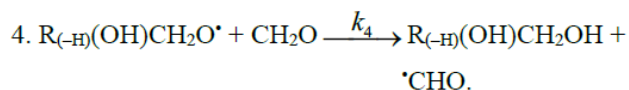
Chain initiation



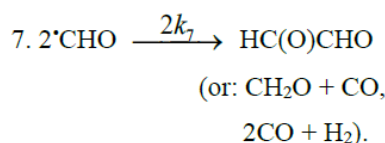
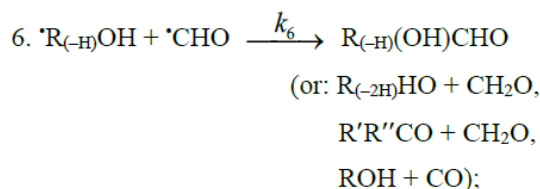
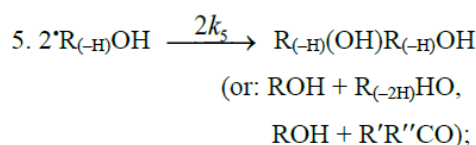
Chain propagation



Inhibition



Chain termination



In these reactions, I is an initiator, e.g., a peroxide [9, 10];

R, some reactive radical (initiator radical); R, an alkyl;

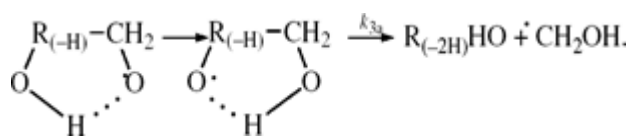
ROH, a saturated aliphatic alcohol, either primary or secondary, beginning from ethanol; CH<sub>2</sub>O, the unsaturated molecule – free formaldehyde;  $\cdot CH_2OH$ , the 1-hydroxymethyl fragment radical;  $\cdot R_{(-H)}OH$ , the reactive 1-hydroxyalkyl addend radical, beginning

from 1-hydroxyethyl;  $R(-H)(OH)CH_2O\cdot$ , the reactive hydroxyalkoxyl 1:1 adduct radical;  $\cdot CHO$ , the low-reactive formyl radical (inhibitor radical);  $ROH$ , the molecular product;  $R(-H)(OH)CH_2OH$ , 1,2-alkanediol;  $R(-2H)HO$ , an aldehyde in the case of a primary alcohol and an  $R'R''CO$  ketone in the case of a secondary alcohol;  $R(-H)(OH)R(-H)OH$ , a vicinal alkanediol;  $R(-H)(OH)CHO$ , a hydroxyaldehyde. The chain evolution stage of *Scheme* includes consecutive reaction pairs 2–3, 2–3a, and 3a–3b; parallel (competing) reaction pairs 3–3a, 3–3b, 3–4, and 3a–4; and consecutive–parallel reactions 2 and 4.

In addition, it seems unlikely that free adduct radicals will add to formaldehyde at higher temperatures the reaction of adding is unlikely because this would result in an ether bond.

The addition of hydroxymethyl radicals to formaldehyde, which is in competition with reaction 3b, is not included as well, because there is no chain formation of ethanediol at 303–448 K [14]. At the same time, small amounts of ethanediol can form via the dimerization of a small fraction of hydroxymethyl radicals, but this cannot have any appreciable effect on the overall process kinetics. The addition of free formyl radicals to formaldehyde cannot proceed at a significant rate, as is indicated by the fact that there is no chain formation of glycol aldehyde in the systems examined [14].

The mechanism of the decomposition of the free adduct radical *via* reaction 3a, which includes the formation of an intramolecular H····O bond and isomerization, can be represented as follows [7, 8, 15]:



The probability of the occurrence of reaction 3a should increase with increasing temperature. This is

indicated by experimental data presented above [7, 8, 15]. The decomposition of the hydroxyalkoxyl radical.  $R(-H)(OH)CH_2O\cdot$  (reaction 3a) is likely endothermic. The endothermic nature of reaction 3a is indirectly indicated by the fact that the decomposition of simple C2–C4 alkoxy radicals  $RO\cdot$  in the gas phase is accompanied by heat absorption: ( $\Delta H = 30\text{--}90 \text{ kJ mol}^{-1}$  [4–6]). Reaction 3b, subsequent to reaction 3a, is exothermic, and its heat for C2–C3 alcohols in the gas phase is  $H_{298} = 40 \text{ to } 60 \text{ kJ mol}^{-1}$  [4–6]. As follows from the above scheme of the process, reactions 3a and 3b, in which the formation and consumption of the highly reactive free radical hydroxymethyl take place (at equal rates under steady-state conditions), can be represented as a single bimolecular reaction 3a,b occurring in a "cage" of solvent molecules.

The free formyl radical resulting from reaction 4, which is in competition with reactions 3 and 3a, is comparatively low-reactive because its spin density can be partially delocalized from the carbon atom *via* the double bond toward the oxygen atom, which possesses a higher electron affinity [3]. For example, in contrast to the methyl and alkoxy  $\pi$ -radicals, the formyl  $\sigma$ -radical can be stabilized in glassy alcohols at 77 K [19]. In the gas phase, the dissociation energy of the C–H bond in formyl radicals is half that for acetyl radicals and is about 5 times lower than the dissociation energy of the  $C_{\alpha}$ -H bond in saturated C1–C3 alcohols [3].

As distinct from reactions 3 and 3a,b, reaction 4 leads to an inefficient consumption of hydroxyalkoxyl adduct radicals, without regenerating the initial 1-hydroxyalkyl addend radicals. Reaction 4 together with reaction 6 (mutual annihilation of free formyl and chain-carrier 1-hydroxyalkyl radicals) causes the inhibition of the nonbranched-chain process. For the disproportionation of the free radicals, the heats of reactions 5–7 for C–C alcohols in the gas

phase vary in the range of  $H = 135$  to  $-385$  kJ mol<sup>-1</sup> [3-6].

The rates of the chain formation of 1,2-alkanediols in reaction 3 (and their nonchain formation in reaction 4), carbonyl compounds in reaction 3a, and methanol in reaction 3b are given by the following equations<sup>1</sup>:

$$V_{3,4}(\text{R}_{(-\text{H})}(\text{OH})\text{CH}_2\text{OH}) = \frac{V_1(\alpha l + x)k_2x}{k_2x^2 + (\alpha l + \beta + x)\sqrt{2k_5V_1}}, \quad (1)$$

$$V_{3a}(\text{R}_{(-2\text{H})}\text{HO}) = V_{3b}(\text{CH}_3\text{OH}) = \frac{V_1\beta k_2x}{k_2x^2 + (\alpha l + \beta + x)\sqrt{2k_5V_1}}, \quad (2)$$

where  $V_1$  is the initiation rate,  $l$  is the molar concentration of the saturated alcohol at the given total concentration  $c_0$  of formaldehyde<sup>2</sup> dissolved in it,  $x$  is the molar concentration of free formaldehyde ( $l \gg x$ ),  $k_2$  is the rate constant of reaction 2 (addition of 1-hydroxyalkyl free radical to free formaldehyde), and  $\alpha = k_3/k_4$  and  $\beta = k_{3a}/k_4$  (mol dm<sup>-3</sup>) are the ratios of the rate constants of the competing (parallel) reactions. Estimates of  $2k_5$  were reported by Silaev *et al.* [22, 24]. From the extremum condition for the reaction 3a rate function,  $V_{3a}/x \rightarrow 0$ , we derived the following analytical expression:

Add .... Under Review

## II. CONCLUSION

In summary, the material on the kinetics of non-branched-chain addition of free saturated 1-hydroxyalkyl radicals to the double bonds of free formaldehyde molecules makes it possible to describe, using Eq. (1) obtained by quasi-steady-state treatment, experimental dependences with a maximum of the formation rates of molecular 1:1

adducts (1,2-alkanediols) on the concentration of an unsaturated compound over the entire region of its change in binary reaction systems consisting of saturated (alcohol) and unsaturated (free formaldehyde) components (Fig. 2).

The proposed addition mechanism involves the reaction of a free hydroxyalkoxyl 1:1 adduct radical with an unsaturated free formaldehyde molecule yielding a low-reactive free formyl radical (the reaction 4 competing with the chain propagation reactions in the *Scheme*). In such binary reaction systems, the unsaturated compound is both a reactant and an autoinhibitor, specifically, a source of low-reactive free radicals shortening kinetic chains.

## III. REFERENCES

- [1]. S. K. Ogorodnikov, *Formal'degid (Formaldehyde)*, Khimiya, Leningrad, 1984.
- [2]. M. M. Silaev, A. V. Rudnev, and E. P. Kalyazin, "Formaldehyde. III. Concentration of Free Formaldehyde as a Function of Temperature, Polarity of Solvents, and Total Concentration of Formaldehyde in Solution", *Zhurnal Fizicheskoi Khimii*, 1979, vol. 53, no. 7, pp. 1647–1651.
- [3]. L. V. Gurvich, G. V. Karachevtsev, V. N. Kondrat'ev, Yu. A. Lebedev, V. A. Medvedev, V. K. Potapov, and Yu. S. Khodeev, "Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu" ("Bond Dissociation Energies, Ionization Potentials, and Electron Affinity"), V. N. Kondrat'ev, Editor, Nauka, Moscow, 1974.
- [4]. S. W. Benson, "Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters", 2nd Edition, Wiley, New York, 1976.
- [5]. J. B. Pedley, R. D. Naylor, and S. P. Kirby, "Thermochemical Data of Organic Compounds", 2nd Edition, Chapman & Hall, London, 1986.

- [6]. Yu. D. Orlov, Yu. A. Lebedev, and I. Sh. Saifullin, "Termokhimiya organicheskikh svobodnykh radikalov" ("Thermochemistry of Organic Free Radicals"), A. M. Kutepov, Editor, Nauka, Moscow, 2001.
- [7]. M. M. Silaev and L. T. Bugaenko, "Kinetics of the Addition of  $\alpha$ -Hydroxyalkyl Radicals to 2-Propen-1-ol and Formaldehyde", *Kinetics and Katalysis*, 1994, vol. 35, no. 4, pp. 509–513, English Translation in: *Kinetics and Katalysis*, 1994, vol. 35, no. 4, 1994, pp. 463–467.
- [8]. M. M. Silaev, "Simulation of Nonbranched Chain Processes for Producing 1,2-Alkanediols in Alcohol-Formaldehyde Systems", *Teoreticheskie Osnovy Khimicheskoi Tekhnologii*, 2007, vol. 41, no. 4, pp. 379–384, English Translation in: *Theoretical Foundations Chemical Engineering*, 2007, vol. 41, no. 4, pp. 357–361.
- [9]. M. Oyama, "A Free-Radical Reaction of Primary and Secondary Alcohols with Formaldehyde", *The Journal of Organic Chemistry*, 1965, vol. 30, no. 7, pp. 2429–2432.
- [10]. G. I. Nikishin, D. Lefor, and E. D. Vorob'ev, "Free Radical Reaction of Primary Alcohols with Formaldehyde", *Izvestiya Akademii Nauk SSSR, Ser. Khimiya*, 1966, no. 7, pp. 1271–1272.
- [11]. W. H. Urry, F. W. Stacey, E. S. Huysen, and O. O. Juveland, "The Peroxide- and Light-Induced Additions of Alcohols to Olefins", *Journal of the American Chemical Society*, 1954, vol. 76, no. 2, pp. 450–455.
- [12]. M. B. Dzhurinskaya, A. V. Rudnev, and E. P. Kalyazin, "High Temperature UV Photolysis of Formaldehyde in Liquid Methanol", *Vestnik Moskovskogo Universiteta, Ser. 2: Khimiya*, 1984, vol. 25, no. 2, pp. 173–176.
- [13]. E. P. Kalyazin, E. P. Petryaev, and O. I. Shadyro, "Reaction between Oxyalkyl Radicals and Aldehydes", *Zhurnal Organicheskoi Khimii*, 1977, vol. 13, no. 2, pp. 293–295.
- [14]. A. I. Novoselov, A.I., Silaev, M.M., and L. T. Bugaenko, "Effect of Temperature on the Yields of Final Products in the  $\gamma$ -Radiolysis of Formaldehyde Solutions in C1–C3 Alkanols", *Khimiya Vysokich Energii*, 2004, vol. 38, no. 4, pp. 270–272, English Translation in: *High Energy Chemistry*, 2004, vol. 38, no. 4, 2004, pp. 236–238.
- [15]. M. M. Silaev and L. T. Bugaenko, "Mathematical Simulation of the Kinetics of Radiation Induced Hydroxyalkylation of Aliphatic Saturated Alcohols", *Radiation Physics and Chemistry*, 1992, vol. 40, no. 1, pp. 1–10.
- [16]. A. I. Novoselov, M. M. Silaev, and L. T. Bugaenko, "Dependence of Ethanediol Yield on Formaldehyde Concentration in  $\gamma$ -Radiolysis of Methanol-Formaldehyde System at 373–473 K", *Khimiya Vysokich Energii*, 2008, vol. 42, no. 1, pp. 74–75, English Translation in: *High Energy Chemistry*, 2008, vol. 42, no. 1, pp. 69–70.
- [17]. A. I. Novoselov, M. M. Silaev, and L. T. Bugaenko, " $\gamma$ -Induced Single-Step Synthesis of Ethylene Glycol from Methanol-Formaldehyde Solution", *Teoreticheskie Osnovy Khimicheskoy Tekhnologii*, 2010, vol. 44, no. 4, pp. 450–453, English Translation in: *Theoretical Foundation of Chemical Engineering*, 2010, vol. 44, no. 4, pp. 432–435.
- [18]. A. I. Novoselov, M. M. Silaev, and L. T. Bugaenko, "Dependence of 1,2-Propanediol Yield on Formaldehyde Concentration in  $\gamma$ -Radiolysis of Ethanol-Formaldehyde System at 373–473 K", *Khimiya Vysokich Energii*, 2007, vol. 41, no. 1, p. 58, English Translation in: *High Energy Chemistry*, 2007, vol. 41, no. 1, p. 53.
- [19]. S. Ya. Pshchetskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. I. Tupikov, "EPR svobodnykh radikalov v radiatsionnoi khimii" ("ESR of Free Radicals in Radiation Chemistry"), *Khimiya*, Moscow, 1972.
- [20]. L. Bateman, "Olefin Oxidation", *Quarterly Reviews*, 1954, vol. 8, no. 2, pp. 147–167.

- [21]. M. M. Silaev, "Simulation of the Nonbranched-Chain Addition of Saturated Free Radicals to Alkenes and Their Derivatives Yielding 1:1 Adducts", *Teoreticheskie Osnovy Khimicheskoi Tekhnologii*, 2007, vol. 41, no. 3, pp. 280–295, English Translation in: *Theoretical Foundations of Chemical Engineering*, 2007, vol. 41, no. 3, pp. 273–278.
- [22]. M. M. Silaev, "Applied Aspects of the  $\gamma$ -Radiolysis of C1–C4 Alcohols and Binary Mixtures on Their Basis", *Khimiya Vysokikh Energii*, 2002, vol. 36, no. 2, pp. 97–101, English Translation in: *High Energy Chemistry*, 2002, vol. 36, no. 2, pp. 70–74.
- [23]. M. M. Silaev, "Estimating the Solvent Concentration in Formaldehyde Solutions at Various Temperatures", *Zhurnal Fizicheskoy Khimii*, 1993, vol. 67, no. 9, p. 1944.
- [24]. M. M. Silaev, L. T. Bugaenko, and E. P. Kalyazin, "On the Possibility of Adequately Estimating of the Rate Constants for the Reaction of Hydroxyalkyl Radicals with Each Other Using the Self-Diffusion Coefficients or Viscosities of the Corresponding Alcohols", *Vestnik Moskovskogo. Univiver-siteta, Ser. 2: Khimiya*, 1986, vol. 27, no. 4, pp. 386–389.
- [25]. J. F. Walker, *Formaldehyde*, Reinhold, New York, 1953, English Translation under the title *Formal'degid*, Goskhimizdat, Moscow, 1957, p. 106.
- [26]. O. I. Shadyro, "Radiation-chemical Conversions of Aldehydes in Various Systems", Ph.D. Thesis (Chemistry), Belarusian State University, Minsk, 1975.
- [27]. M. M. Silaev, "Relative Reactivity of  $\alpha$ -Hydroxyethyl Radicals for 2-Propene-1-ol and Formaldehyde Double-Bond Addition", *Vestnik Moskovskogo Universiteta, Ser. 2: Khimiya*, 1993, vol. 34, no. 3, p. 311.
- [28]. H. Seki, R. Nagai, and M. Imamura, " $\gamma$ -Radiolysis of a Binary Mixture of Methanol and Water. The Formation of Formaldehyde in the Radiolysis of Liquid Methanol", *Bulletin of the Chemical Society of Japan*, 1968, vol. 41, no. 12, pp. 2877–2881.

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**Appendix**

Table. The experimental concentrations  $x$  (mol dm<sup>-3</sup>) of free formaldehyde at different temperatures  $T$  (K) and total formaldehyde concentrations  $c_0$  (mol dm<sup>-3</sup>) in various solvents

$c_0$	$T$	$10^2x$	$c_0$	$T$	$10^2x$	$c_0$	$T$	$10^2x$	$c_0$	$T$	$10^2x$
<b>Water</b>			4.44	389	5.20	4.0	381	5.00	1.8	371	2.08
1.0	358	0.78	4.44	405	7.50	4.0	397	8.80	1.8	393	6.00
1.0	387	2.22	4.44	418	10.0	4.0	409	12.00	1.8	418	12.20
1.0	393	3.23	<b>Methanol</b>			6.2	347	2.80	1.8	438	16.70
1.0	407	4.55	1.0	375	0.33	6.2	376	7.80	3.0	343	1.25
2.0	353	1.44	1.0	395	1.00	6.2	393	12.50	3.0	375	5.40
2.0	387	4.70	1.0	423	2.90	<b>1-Propanol</b>			3.0	403	15.80
2.0	397	6.60	2.5	373	0.60	1.0	371	0.83	3.0	413	19.40

2.0	407	8.55	2.5	385	1.15	1.0	393	2.10	5.6	343	2.80
4.0	343	0.78	2.5	398	1.80	1.0	413	4.30	5.6	358	3.35
4.0	363	2.33	5.4	351	0.78	1.0	435	7.65	5.6	363	5.80
4.0	385	6.45	5.4	383	3.70	1.9	353	0.70	5.6	371	6.50
4.0	403	8.90	5.4	398	6.80	1.9	383	3.06	5.6	383	12.10
4.0	413	11.10	7.0	365	4.70	1.9	405	7.65	<b>2-Methyl-2-propanol</b>		
6.0	351	2.22	7.0	383	12.50	1.9	417	11.70	1.0	347	1.20
6.0	375	6.70	7.0	391	16.00	4.0	349	1.67	1.0	367	4.50
6.0	389	10.70	<b>Ethanol</b>			4.0	373	6.10	1.0	387	11.00
6.0	398	14.10	1.0	367	0.33	4.0	393	13.30	1.0	398	19.30
8.4	364	5.50	1.0	387	0.67	6.0	338	1.39	2.0	335	1.10
8.4	376	8.32	1.0	397	1.45	6.0	357	5.00	2.0	357	4.30
8.4	388	10.97	1.0	413	2.70	6.0	377	11.70	2.0	375	13.00
<b>Ethenediol</b>			1.0	423	4.00	6.0	389	18.30	2.0	383	18.50
1.0	409	1.30	2.0	373	1.10	7.8	343	3.06	3.0	338	1.70
1.0	418	1.80	2.0	394	2.90	7.8	358	6.25	3.0	353	4.70
1.0	435	2.45	2.0	409	5.80	7.8	377	16.90	3.0	365	9.60
3.33	358	1.20	2.0	419	8.20	<b>2-Propanol</b>			3.0	373	15.50
3.33	387	3.30	3.0	361	1.20	1.0	365	0.98	6.0	345	6.90
3.33	401	5.10	3.0	387	3.70	1.0	393	3.05	6.0	351	9.00
3.33	415	7.20	3.0	409	7.80	1.0	411	6.00	6.0	361	13.40
4.44	338	1.00	4.0	355	2.30	1.0	433	10.40	6.0	365	18.30