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### ARTICLE



### Interaction of triols with formaldehyde and acetone: Experimental and theoretical study

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#### Abstract

Experimental and theoretical aspects of the condensation of glycerol and its homologs (1,2,3- and 1,2,4-butanetriols) with formaldehyde and acetone are studied under conditions of acid catalysis. Calculation of the thermodynamic parameters of the resulting products by the composite method CBS-QB3 shows that the six-membered heterocycles, the products of the interaction of triols with formaldehyde, are thermodynamically more stable than the five-membered acetals, while the reaction of the same triols with acetone is preferable for the formation of the five-membered acetals. This is due to the fact that the regioselectivity of the studied reactions is determined by the structural features and reactivity of the carbocations formed in a condensed medium during the course of the reaction. According to the theoretical data obtained experimentally, during the condensation of glycerol and 1,2,4-butanetriol with formaldehyde in the most stable form of the six-membered cyclic carbocation, intramolecular hydrogen bonding and anomeric stabilization due to the axially oriented hydroxyl group take place. As a result, cation 1b-1 is 1.2-1.6 kJ/mol more stable than its five-membered isomers (1a-1 and 1b-2). It leads to the predominant formation of 1,3-dioxane (3b). However, upon condensation of butanetriol-1,2,3 with formaldehyde, the intermediate cation 4a-1 turns out to be significantly more stable than the other isomers due to the strong intramolecular hydrogen bond in the six-membered ring with the participation of the hydroxyl group of the substituent and the hydroxyl group of the cationic center, leading to the predominant formation of the dioxolane 6a.

**KEYWORDS** 

acetals, DFT calculations, polyols

#### INTRODUCTION 1

The products of interaction of alcohols with carbonyl compounds—acetals—are a type of ethers that are widely used in organic synthesis (to protect the carbonyl groups of organic molecules from the action of bases, Grignard reagents, lithium aluminum hydride, oxidizers),<sup>[1,2]</sup> in perfumery as fragrant substances,<sup>[3]</sup> as additives to beverages and food products (emulsifiers),<sup>[4]</sup> and in pharmaceuticals as a solvent.<sup>[5]</sup> Recently, acetals of

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polyols—glycerol and sugars—have been proposed as additives to improve the properties of motor fuels.<sup>[6-10]</sup>

Ethers are in many respects more preferred components of fuels than alcohols. The main advantages are their higher oxidative stability, heat of combustion, as well as a more favorable interphase distribution in the water-fuel system. An important property of a variety of ethers (acetals) is the possibility of obtaining them from renewable sources (biomass, agricultural and forestry waste, food industry, etc.). The presence of oxygen esters in the composition can significantly improve the environmental performance of engines operating on these alternative motor fuels. It should be noted that some ethers have very high octane and cetane numbers,<sup>[11]</sup> have a low pour point, have good lubricating properties, and also reduce harmful emissions from the combustion of motor fuels.<sup>[12]</sup> Convenient polyols for the production of acetals are glycerol and its homologs (1,2,3- and 1,2,4-butanetriols).

The process of acetalization of polyols proceeds under conditions of acid catalysis and relates to the proton transfer (PT) reaction, one of the most important transformations in chemistry and biology, which contributes to the foundation of science. That is why the PT reaction has been very actively studied recently, including using the methods of quantum chemistry. Most of current reports on excited-state proton transfer (ESIPT) process are mainly the excited-state intramolecular or intermolecular PT reaction along with one hydrogen-bonding wire. That is to say, the ESIPT process incorporating the transfer of two or more protons should be of paramount interest. Such multiple PT compounds are rare and usually involve molecular self-assembly or solvent assistance.<sup>[13-16]</sup>

In this work, the experimental and theoretical aspects of the acetalization/ketalization of glycerol and its homologs under conditions of acid catalysis are considered.

#### 2 | RESULTS AND DISCUSSION

The thermodynamic parameters of the products of interaction of triols **1**, **4**, and **7** with formaldehyde and acetone were calculated using the CBS-QB3 composite method<sup>[17,18]</sup> in order to establish the general regularities of the transformations under study (Scheme 1).

The theoretical results presented in Scheme 1 show that the products of interaction of triols 1, 4, and 7 with acetone-the five-membered acetals 2a, 5a, 5c, and 8aare thermodynamically more stable than the sixmembered acetals 2b, 5b, and 8b. On the contrary, in the reaction of the same triols with formaldehyde, the formation of the six-membered heterocycles 3b, 6b, and 9b is preferred. When carrying out the reactions, it was noted that glycerol 1 under acid catalysis conditions selectively reacts with acetone to form (2,2-dimethyl-1,3-dioxolan-4-yl) methanol 2a (solketal) in quantitative yield, and with a solution of formaldehyde with similar conditions to the formation of a mixture of two isomers 1,3-dioxolan-4-yl-methanol 3a and 1,3-dioxan-5-ol 3b (yield 95%, Scheme 1, Equation 1) in the ratio 3a/ 3b = 1:1.5 according to the spectra of nuclear magnetic resonance (NMR spectroscopy). The ratio of isomeric heterocycles 3a and 3b was determined by the signal intensity of methylene protons of the C(2) atom of the heterocyclein <sup>1</sup>H NMR spectra.<sup>[19]</sup> The above results are consistent with the generally accepted concepts outlined in a review<sup>[20]</sup> of the predominant formation of five- and six-membered ring compounds in the condensation reaction of alcohols and carbonyl compounds. We note that in the cited work, a conclusion was drawn on the kinetic control of the formation of five-membered cycles, whereas the formation of dioxanes is due to their greater thermodynamic stability.



**SCHEME 1** Transformations studied and the Gibbs free energy ( $\Delta G^{\circ}$ , kJ/mol) for the condensation reactions of triols **1**, **4**, and **7** with formaldehyde and acetone

Condensation of 1,2,3-butanthriol 4 with acetone leads to a mixture of five-membered ketals 2,2-dimethyl-4- $\alpha$ -hydroxyethyl-1,3-dioxolane **5a** and 2,2,4-trimethyl-5-hydroxyethyl-1,3-dioxolane 5c in the form of cis/trans isomers in 1:1 ratio (according to NMR) with a predominant (90%) content of compound 5a, whereas 2,2,4-trimethyl-5-hydroxy-1,3-dioxane 5b was not detected in the reaction mass (Scheme 1, Equation 2). The interaction of this triol 4 with formaldehyde also proceeds with the predominant formation of five-membered formals, despite the fact that, from the point of view of thermodynamics, compound **6b** is more stable than structures **6a** and **6c**. Three cyclic isomers,  $4-\alpha$ -hydroxyethyl-1,3-dioxolane 6a, 4-methyl-5-hydroxyethyl-1,3-dioxolane 6c (cis/trans ratio 1:1 ratio) and 4- methyl 5-hydroxy-1,-3-dioxane **6b** (cis/trans ratio 1:1), are in the ratio of **6a**/ 6b/6c = 3:1: 0.5 (according to NMR spectroscopy). Most likely, the observed correspondences are explained by different reaction mechanisms: namely, for the case described, the kinetic control of the reaction is essential. The homolog of glycerol, 1,2,4-butanetriol 7, in reactions with formaldehyde and acetone, behaves similarly to glycerol.<sup>[19]</sup> In the case of acetone, 2,2-dimethyl-4-hydroxyethyl-1,3-dioxolane 8a is selectively formed with a yield of 90%, and the condensation of triol 7 with formaldehyde leads to the formation of a mixture of fiveand six-membered formals 1,3-dioxolane 9a and 1.3-dioxane 9b, in which 1.3-dioxane 9b prevails (the ratio 9a/9b = 1:4 according to NMR spectroscopy). It should be noted that the formation of 1.3-dioxepan-5-ol **9c** is observed in trace amounts (Scheme 1, Equation 3).

Analyzing the results obtained as a whole, one can note the good agreement between theory and experiment for the case of the interaction of triols with acetone. At the same time, the evaluation of only the thermodynamic parameters of the reaction products cannot describe all the experimentally observed features of the condensation of triols with formaldehyde. We assumed that the explanation of the observed contradictions lies in the specific features of the structure and reactivity of the carbocations formed in the condensed medium during the course of the studied reactions. When the studied triols react with formaldehyde in nonpolar solvents and acidic medium, one should take into account the possible transformation of primary and/or secondary hydroxyl groups of a triol into the corresponding cations (Schemes 2–4).

#### 2.1 | Glycerol

The condensation of glycerol with formaldehyde proceeds through the formation of cations **1a** and **1b** (Scheme 2). The presence of several single bonds in the



**SCHEME 2** Cationic intermediates of acid-catalyzed condensation of glycerol with formaldehyde. The Gibbs free energies ( $\Delta G^{\circ}$ , kJ/mol) of cyclic intermediates formed spontaneously as a result of the free rotation of cations **1a** and **1b** around the C–C bond axes are given



**SCHEME 3** Cationic intermediates of acid-catalyzed condensation of butanetriol-1,2,3 with formaldehyde. The Gibbs free energies ( $\Delta G^{\circ}$ , kJ/mol) of the cyclic intermediates formed spontaneously as a result of the free rotation of cations **4a–c** around the C–C bond axes are given



**SCHEME 4** Acyclic cationic intermediates of acid-catalyzed condensation of butanetriol-1,2,3 with formaldehyde

cation causes the existence of a set of states whose energy is determined by the conformational potential typical of aliphatic alcohols. In addition, some conformations will be further stabilized by the formation of intramolecular hydrogen bonds. However, the main factor in the extrastabilization of conformers **1a** and **1b** is the Coulomb interaction of the cationic center with the lone electron pairs of one of the neighboring oxygen atoms. These

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			0 <b>_</b> ⊕ 1a	1b					
Initial conformation	φ1 (º)	φ2 (º)	<i>r</i> (01-C) Å	r(0-C) Å	$\Delta G^{\circ}$ , <sup>a</sup> kJ/mol	Cycle on Scheme 2			
1a									
ap,ap	174.9	150.6	4.20	1.61	-1.9	1a–1			
ap,+sc	-145.6	46.9	1.59	3.97	-7.5	1a-1			
ap,-sc	-148.9	-57.2	1.59	4.54	-2.7	1a-1			
+sc,ap	53.4	148.0	4.61	1.59	-1.0	1a-1			
+ <i>sc</i> ,+ <i>sc</i>	63.9	56.5	4.62	3.88	23.4				
+ <i>sc</i> , – <i>sc</i>	52.9	-78.0	4.70	4.42	30.5				
-sc,ap	-46.8	145.6	3.97	1.59	-7.5	1a-1			
-sc,+sc	-74.1	46.8	2.65	3.70	7.7				
- <i>SC</i> , - <i>SC</i>	-42.4	-47.0	4.15	4.61	23.1				
1b									
ap,ap	-176.8	177.3	5.14	2.60	0.0				
ap,+sc	-179.5	60.2	5.24	4.07	20.4				
ap,-sc	-172.2	-67.3	5.25	4.41	24.5				
+sc,ap	55.7	174.3	4.99	2.53	1.1				
+ <i>sc</i> ,+ <i>sc</i>	62.5	-22.8	1.64	4.12	-2.3	1b–1			
+ <i>sc</i> , - <i>sc</i>	62.5	-22.8	1.64	4.12	-2.4	1b–1			
-sc,ap	-50.6	138.6	3.37	1.57	-9.0	1b-2			
-sc,+sc	-52.2	55.5	1.61	3.52	-8.8	1b–1			
-scsc	-61.9	-65.8	4.82	4.50	16.0				

TABLE 1 Main geometrical parameters and relative Gibbs free energies of rotation isomers of cations 1a and 1b

<sup>a</sup>Standard Gibbs energies of conformers with respect to *ap,ap*-form of cation **1b**. The calculated values correspond to local minima on conformational PES. The

values of  $\Delta G^{\circ}$  for global minima of cyclic cations are shown on Scheme 2.

factors form the distribution of conformers by relative stability and explain the patterns of product formation.

Table 1 contains the results of calculations of geometric parameters and Gibbs energies of conformers 1a and **1b**, which are formed during the free rotation along the  $\varphi$ 1 and  $\varphi$ 2 axes. In some conformations, the carbocation is favorably oriented with respect to the lone electron pair of one of the oxygen atoms of the triol, which leads to spontaneous cyclization. At the same time, some relatively stable conformers of cations are not capable of spontaneously cyclizing and play the role of "reservoirs" of cationic states. Cyclic forms of cations can either undergo a reversible opening of the cycle or be additionally stabilized by intramolecular hydrogen bonds or an anomeric effect, or they can split off a proton to form molecular reaction products. In particular, during the condensation of glycerol with formaldehyde,

intramolecular hydrogen bond and anomeric stabilization take place due to an axially oriented hydroxyl group in the most stable form of a six-membered cyclic carbocation. As a result, the cation **1b–1** is 1.2–1.6 kJ/mol more stable than its five-membered isomers (**1a–1** and **1b–2**). Apparently, this fact explains the predominant formation of 1,3-dioxane (**3b**) (Scheme 1).

#### 2.2 | Butanetriol-1,2,3

When butanetriol-1,2,3 condenses with formaldehyde, the formation of three types of cations is possible (Scheme 3). The result of free rotation through two single C–C bonds is the formation of various heterocyclic cations, the relative energies of which are listed in Table 2. As in the previous case, conformational rotation can lead to a set of cation

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	HO <sub>1</sub>	¢1 ¢2/ ОН				
		4a '''	4b		4c	
Initial conformation	φ1 (°)	φ2 (°)	<i>r</i> (01-C) Å	r(0-C) Å	$\Delta G^{\circ}$ , a kJ/mol	Cycle on Scheme 3
4a						
ap,ap	174.9	147.0	4.19	1.57	-4.5	4a-2
ap,+sc	-145.4	48.5	1.59	3.94	0.4	4a-1
ap,-sc	-150.8	-54.2	1.59	4.52	6.3	4a-1
+sc,ap	57.9	144.5	4.64	1.55	-4.4	4a-2
+ <i>sc</i> ,+ <i>sc</i>	64.8	58.7	4.66	3.76	33.2	
+ <i>sc</i> , - <i>sc</i>	80.9	-55.6	4.42	4.58	40.5	
-sc,ap	-48.5	143.5	3.96	1.56	-10.5	4a-2
-sc,+sc	-78.3	46.4	1.50	2.96	-22.6	4a-1
- <i>SC</i> , - <i>SC</i>	-53.9	-64.0	4.18	4.43	38.2	
4b						
ap,ap	-172.4	174.9	5.07	2.57	5.5	
ap,+sc	-177.0	58.8	5.18	4.07	28.6	
ap,-sc	-167.4	-77.8	5.30	4.27	33.5	
+sc,ap	56.0	178.0	4.99	2.56	11.8	
+ <i>sc</i> ,+ <i>sc</i>	60.9	-29.5	1.60	4.08	2.6	4b-2
+ <i>sc</i> ,- <i>sc</i>	60.9	-29.5	1.60	4.08	2.6	4b-2
-sc,ap	-49.4	173.5	4.34	2.43	7.2	
-sc,+sc	-51.6	56.6	1.58	3.53	-12.3	4b-2
- <i>SC</i> , - <i>SC</i>	-42.3	-56.0	4.35	4.57	33.2	
4c						
ap,ap	-172.6	174.5	5.08	2.56	0.0	
ap,+sc	177.6	57.2	5.10	4.10	18.8	
ap,-sc	-176.2	-68.3	5.93	4.40	25.0	
+sc,ap	62.7	144.6	5.36	1.60	0.7	4c-1
+ <i>sc</i> ,+ <i>sc</i>	42.5	15.6	1.68	4.10	4.7	4c-2
+ <i>sc</i> , <i>-sc</i>	64.5	-23.2	1.65	4.12	3.4	4c-1
-sc,ap	-51.6	137.8	3.35	1.57	-8.2	4c-1
- <i>sc</i> ,+ <i>sc</i>	-53.9	56.6	1.62	3.51	-7.8	4c-2
- <i>SC</i> , - <i>SC</i>	-74.5	-67.0	5.08	4.47	20.1	

#### TABLE 2 The main geometrical parameters and relative Gibbs free energies of rotation isomers of cations 4a-c

<sup>a</sup>Standard Gibbs energies of conformers with respect to *ap,ap*-form of cation **4c**. The calculated values correspond to local minima on conformational PES. The values of  $\Delta G^{\circ}$  for global minima of cyclic cations are shown on Scheme 3.

states that differ in the presence or absence of stabilization factors: the formation of a C—O bond with a ring closure, a six-membered cycle of "chair" or "bath" conformation, hydrogen bonding, anomeric stabilization, etc.

It is interesting to note that no conformations capable of spontaneous cyclization into the dioxolane structure were found in the case of cation **4b**. In general, the conformational potential of **4a–c** is expectedly similar to that of cations generated from glycerol. A significant difference was found for cation **4a–1**, which turned out to be significantly more stable than other isomers due to the strong intramolecular hydrogen bond in the fivemembered cycle with the participation of the hydroxyl group of the substituent (hydrogen bond acceptor) and the hydroxyl group of the cationic center (hydrogen bond donor). Apparently, this type of specific stabilization of cations causes excessive accumulation of dioxolane **6a** in the spectrum of the condensation products of butanetriol-1,2,3 with formaldehyde (Scheme 1), despite the lower thermodynamic stability of this compound compared to the derivative of 1,3-dioxane.

#### 2.3 | Butanetriol-1,2,4

When butanetriol-1,2,4 condenses with formaldehyde, it is also possible to form three types of carbocations (Scheme 4). Free rotation in carbocations **7a–c** can lead to structures capable of spontaneous cyclization, with the formation of five-, six-, and seven-membered heterocyclic cations. The presence of the third axis of rotation at a single C–C bond significantly complicates the conformational analysis, since there are 27 possible rotation isomers for each cation.

However, it should be noted that, first, there is a good agreement between the relative yields of reaction products 9a-c and their thermodynamic stability (Scheme 1), which indicates the thermodynamic control of the reaction. Second, the formation of a seven-membered cycle is associated with significant entropy losses compared with the formation of five- and six-membered cycles. For this reason, a conformational analysis of the cations 7a-c appears redundant and was not performed.

#### **3** | EXPERIMENTAL

#### 3.1 | 3.1 Materials

In the work, we used commercially available reagents glycerol 1,2,3-butanetriol, 1,2,4-butanetriol, acetone, and benzene. The method of synthesis and the physico-chemical characteristics of ketals, glycerol **1** and 1,2,4-butanetriol **7** are described elsewhere.<sup>[19,21]</sup>

# 3.2 | Synthesis of 1,2,3-butanetriol ketals 5a-c

A mixture of 5 g (0.04 mol) of 1,2,3-butanthriol, 2.5 g (0.04 mol) of acetone, and 10 wt% *p*-toluenesulfonic acid was stirred at room temperature for 5 hr. Then 4 g (anhydrous)  $K_2CO_3$  was added and continued stirring for 1 hr. The mixture was filtered and concentrated, and the

residue was distilled in vacuum (85°C, 8 Torr). Yield 5.5 g (90%).

## 3.3 | Synthesis of 1,2,3-butanetriol formals 6a–c

A mixture of 5 g (0.04 mol) of 1,2,3-butanetriol, 1 g (0.03 mol) of paraform, 30 ml of anhydrous benzene, and 1% by weight of sulfuric acid was boiled until the calculated amount of water (0.7 ml) was separated. After completion of the reaction (3–4 hr), the solution was cooled and evaporated. The residue was distilled under vacuum (83°C, 10 Torr). Yield 3.5 g (70%).

#### 3.4 | NMR analysis

<sup>1</sup>H, <sup>13</sup>C NMR spectra were acquired on a Bruker Avance III spectrometer (500 and 125 MHz, respectively) in CDCl<sub>3</sub>. TMS (0.05%) was used as the internal standard for <sup>1</sup>H and <sup>13</sup>C NMR spectra. The assignment of signals in the NMR spectra was based on <sup>1</sup>H–<sup>1</sup>H (COSY), <sup>1</sup>H–<sup>13</sup>C (HSQC, HMBC) 2D correlations. <sup>13</sup>C NMR spectra were registered in DEPT-90, DEPT-135, and complete proton suppression modes.

#### 3.5 | Mass spectroscopy

Chromato-mass spectra were recorded on a "Chromatek Crystal 5000.2" instrument with a capillary quartz column of 30 m, an analysis time 20 min, an ion source temperature 260°C, a transition line temperature 300°C, a scan range 30–300, pressure 37–43 mTorr, temperature 80–300°C, temperature of the input port 320°C, carrier flue gas helium, and heating rate 20°/min. To obtain the mass spectra of the compounds, electron impact ionization method was used.

#### 3.6 | Calculation procedures

All theoretical calculations were performed using the GAUSSIAN 09 software. Revision C1.<sup>[22]</sup> To optimize the structural parameters of reagents, intermediates, and products of the condensation of triols with acetone and formaldehyde, as well as to perform frequency calculations, the composite method CBS-QB3 was used.<sup>[17,18]</sup> Thermodynamic parameters of the reactions studied were calculated for the experimental conditions of temperature 298.15 K and pressure 1 atm. The effect of solvents

(acetone, benzene, and toluene) on the energies of the reaction participants was taken into account using the polarized continuum model.<sup>[23]</sup> For a number of cationic systems, a procedure for relaxing scanning the potential energy surface was performed using the B3LYP density functional<sup>[24]</sup> with the CBSB7 basis set<sup>[17]</sup> by varying the torsion angles corresponding to the rotation of cation species around single C–C bonds. All possible isomers of the reaction products were examined (Data S1). In addition, the NMR screening tensors were calculated using the continuous set of gauge transformations<sup>[25,26]</sup> and the B3LYP and TPSS density functionals.<sup>[27,28]</sup> These results are also presented in Data S1.

#### 4 | CONCLUSIONS

A theoretical analysis of the formation patterns of condensation products of triols with acetone and formaldehyde allowed us to draw the following conclusions. First, the correspondence between the calculations and experiment points to the thermodynamic control of the reaction, during which a set of equilibrium transformations involving cationic intermediates leads to the thermodynamically most stable reaction products. Second, the condensation of triols with formaldehyde proceeds less unambiguously. In particular, during the transformation of butanetriol-1,2,3, it is necessary to take into account the spectrum of possible cationic states that differ in their reactivity and stability, which ultimately leads to the preferential accumulation of product **6a** instead of the derivative of 1,3-dioxane expected by thermodynamic stability.

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#### SUPPORTING INFORMATION

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