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QUANTUM CHEMICAL INVESTIGATION BY THE AM1 METHOD OF THE CATALYTIC CYCLODEHYDRATION OF 1,4-BUTANEDIOL

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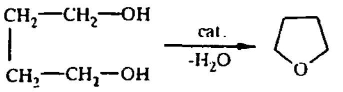
1,4-Butanediol is converted into tetrahydrofuran in the presence of silica gel at temperatures of 245-340°C. The mechanism of the conversion of 1,4-butanediol has been studied by the quantum chemical AM1 method with full optimization of the geometry. It was established that two parallel reactions are possible depending on the conformation of the molecule. The cyclodehydration reaction is effected by conversion of a semicyclic conformer of the protonated diol molecule at a basic center of the catalyst by a concerted mechanism. The heat of the reaction forming tetrahydrofuran is −161.768 kcal/mole.

The conversion of 1,4-butanediol into tetrahydrofuran is an industrial process which is effected under conditions of acid-base catalysis [1]:



The dehydration−cyclization reaction of 1,4-butanediol is accelerated by catalytic amounts of mineral acids (H_2SO_4, H_3PO_4), certain Lewis acids ($PdCl_2$), and heterogeneous catalysts (silica gel, aluminosilicates, synthetic zeolites) [2-4]. Tetrahydrofuran is the main conversion product of 1,4-butanediol in the vapor phase at 245-340°C in the presence of silica gel and kieselguhr (Table 1). When using certain forms of silica gel as catalyst, the yield of tetrahydrofuran was 100%. In addition to tetrahydrofuran, the presence of 4-hydroxybutanal and 2,3-dihydrofuran has been established in the reaction products formed on dehydrogenation of 1,4-butanediol. As is known, the dehydration of alcohols characteristically uses the acid properties of the catalyst. From the results given in Table 1, it follows that the surfaces of the silica gels investigated in this work differ significantly in the concentration of reactive acidic centers.

Several possible reaction mechanisms for the cyclodehydration of diols have been discussed in the literature [4-7]. The suggestion has been made that Lewis acids form donor−acceptor bonds with the hydroxyl groups and induce synchronous elimination of water molecules and the cyclization reaction. According to another version, tetrahydrofuran is formed by the sequence of adsorption of diol onto Brönsted acid centers, protonation by one of the hydroxyl groups, removal of a water molecule with the formation of a carbocation, and cyclization. Experimental data obtained for monoalkanols [8] are used as a basis for the suggestion regarding carbocation formation. Bartok and coworkers considered that the intramolecular cyclization of 1,4-butanediol occurs as a result of attack of a protonated OH group on a second hydroxyl group and belongs to the S_N2 type of substitution reactions [5].

Our investigations by quantum chemical methods showed that on full optimization of the geometry of the linear carbocation obtained by the dehydration of protonated 1,4-butanediol, it is possible to form an intermediate cyclic positively charged complex [7]. A similar complex was included in an empirical scheme for the mechanism when considering the con-

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TABLE 1. Vapor Phase Conversion of 1,4-Butanediol

Catalyst	Reaction temperature, °C	Conversion, %	Yield, %		
			tetrahydrofuran	4-hydroxybutanal	2,3-dihydrofuran
Silica gel*	245	2,5	0,8	0,2	0,3
	270	2,2	0,6	0,2	0,4
	300	9,8	3,6	0,3	3,0
Silica gel L†	245	100	99,0	—	—
Silica gel	260	100	100	—	—
KSM [3]	340	100	99,5	—	—
Silica gel	300	100	99,3	—	—
KSM [3]	340	100	99,3	—	—
Kieselguhr	245	18,7	6,7	1,0	2,2
	270	7,7	5,0	0,7	1,2
	300	17,2	11, 8	2,3	1,5

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*From Acros.
†From Chemapol.

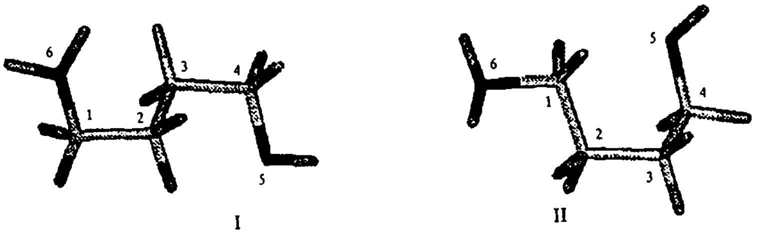


Fig. 1. Conformers of protonated 1,4-butanediol.

version of the diol in the presence of CrZSM-5 catalyst [6]. In the opinion of the authors, the structure of the pores of the zeolite catalyst used by them was favorable for the stabilization of the intermediate cyclic compounds.

The role of the basic centers of the silica gel in the conversion of 1,4-butanediol has been investigated by the AM1 quantum chemical method in the present study.

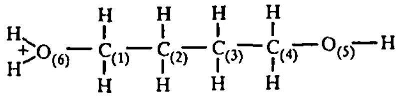
The 1,4-butanediol molecule is known to have a large number of conformers [9]. Two conformers (Fig. 1) of protonated 1,4-butanediol (I) ($E_{tot} = -1297.655$ eV) and (II) ($E_{tot} = -1297.784$ eV) were used in the present investigation to refine the mechanism for the conversion of 1,4-butanediol into tetrahydrofuran. The torsion angles of these conformers are given in Table 2.

The distance between the $C_{(1)}$ and $O_{(5)}$ atoms in conformer (II) is 2.629 Å. The maximum barrier to rotation about the $C_{(1)}-C_{(2)}$ and $C_{(2)}-C_{(3)}$ bonds on converting conformer (I) to conformer (II) is 1.223 kcal/mole.

Like the generally accepted view on heterogeneously catalyzed dehydration of alcohols [10], it is assumed in the present work that one of the OH groups of the diol, adsorbed onto an acidic center of the catalyst, participates in the formation of a surface complex of the oxonium ion type. Calculations showed that the subsequent conversion of the oxonium ion of the 1,4-butanediol depends on its conformation. Thus, if the protonated 1,4-butanediol is adsorbed in conformation (I) on the surface and the unprotonated hydroxyl group of the surface complex is in the vicinity of a basic $Si(OH)_3O^-$ center then the group gives away its proton to the catalyst and is converted into the unsaturated alcohol $CH_2=CH-CH_2-CH_2-OH$. The heat of conversion of conformer (I) is −167.746 kcal/mole. Visualization of the results of optimizing the catalyst−reactant systems makes it possible to establish that the conversion of conformer (I) may be divided into several steps, which is most interesting from our point of view in understanding the reaction mechanism (Fig. 2).

In the initial state (a) the distance between the hydroxyl group and the basic center is 1.266 Å. After loss of hydroxyl group proton to the catalyst (b, optimization cycle 23) the formation occurs of a five-membered ring with the participation of one of the hydrogen atoms at $C_{(2)}$ and oxygen $O_{(5)}$ (cycle 24, not shown in Fig. 2), then fission of the $C-OH_2^+$ bond and dehydration follow (c, cycle 25). Breaking of the $C_{(2)}-H$ bond is observed in cycle 27 with the formation of the unsaturated alcohol 3-buten-1-ol (d). The length of the $C_{(2)}-H$ and $H-O_{(5)}$ bonds in the transition state (cycle 25) are 1.451 and 1.341 Å respectively. The angle $C_{(2)}-H-O_{(5)}$ is 129.282°. The length of the $C_{(1)}-C_{(2)}$ bond in the resulting unsaturated alcohol at 1.332 Å corresponds to the experimentally established value for the length of a $C_{sp2}=C_{sp2}$ bond [11]. It was shown for con-

TABLE 2. Torsion Angles in Conformers (I) and (II)



$H_2\overset{+}{O}_{(6)}-C_{(1)}H_2-C_{(2)}H_2-C_{(3)}H_2-C_{(4)}H_2-O_{(5)}-H$

Sequence of atoms forming the torsion angle	Torsion angle (deg)	
	conformer I	conformer II
$O_{(6)}-C_{(1)}-C_{(2)}-C_{(3)}$	-86,1	-174,7
$C_{(1)}-C_{(2)}-C_{(3)}-C_{(4)}$	-176,4	-60,0
$C_{(2)}-C_{(3)}-C_{(4)}-O_{(5)}$	53,6	64,7

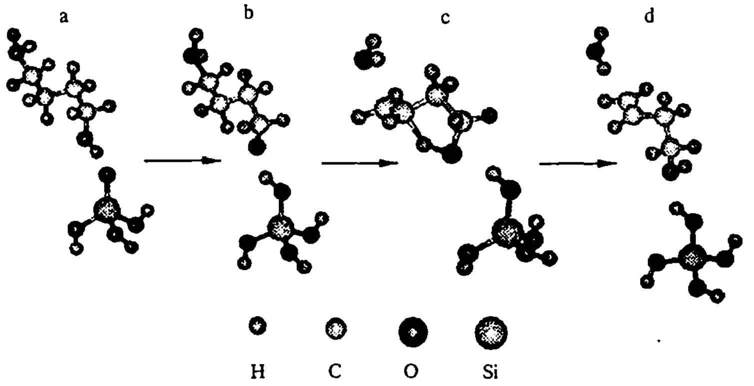


Fig. 2. Conversion of conformer (I).

former (II) that if the oxonium ion of 1,4-butanediol, migrating across the catalyst surface, is drawn by an unprotonated OH group to a basic center at a distance greater than 1.40 Å then the molecule is turned towards this center by its positively charged OH_2^+ group and is deprotonated. If again the molecule in the initial state is orientated relative to the catalyst surface in such a way that the distance between the basic center and the hydroxyl group is less than 1.40 Å (1.373 Å, for example) then according to our calculations, this leads to the formation of tetrahydrofuran. The initial state (*a*) and three cycles of the conversion process of the semicyclic conformer (II) (b, c, d) are represented in Fig. 3. In this case, after loss of the hydroxyl group proton to the catalyst (b, cycle 25), fission of the $C-OH_2^+$ bond follows, then dehydration (c, cycle 26), and formation of the furan ring (d, cycle 27). The heat of the reaction is −161.768 kcal/mole. The indicated conversions of the diol take place without activation barriers, as shown by the character of the change of heat of formation of the reaction system in each cycle of the optimization process (Fig. 4).

This makes it possible to conclude that a concerted, close to synchronous, mechanism probably operates in the cyclodehydration of a protonated 1,4-butanediol.

The presence of a potential barrier of height 1.152 kcal/mole on approach of a reacting protonated 1,4-butanediol molecule [conformation (II)] to the catalyst is established only at a change of distance from 1.40 to 1.373 Å. The reaction coordinates method was used to calculate the potential barrier. The distance between the basic center and the hydroxyl group was selected as reaction coordinate. The scanning step was 0.02 Å.

The following circumstance attracts attention. Although conformer (II) is more stable than conformer (I), according to calculation the heat of conversion of conformer (II) into reaction products is somewhat less than the corresponding heat for conformer (I). This leads to the assumption that the reaction products described above (3-buten-1-ol and tetrahydrofuran) must be formed in comparable amounts in the presence of catalysts containing SiO_2. However, under actual conditions, including our experiments on the investigation of converting 1,4-butanediol in the presence of certain forms of silica gel (see Table 1), the selectivity towards tetrahydrofuran approaches 100% and the unsaturated alcohol was not found in the reaction mixture. This apparent inconsistency is probably linked with the special features of the structure of the catalyst active surface, due to which the mutual disposition of clusters containing acidic and basic centers is more favorable for the cyclodehydration reaction.

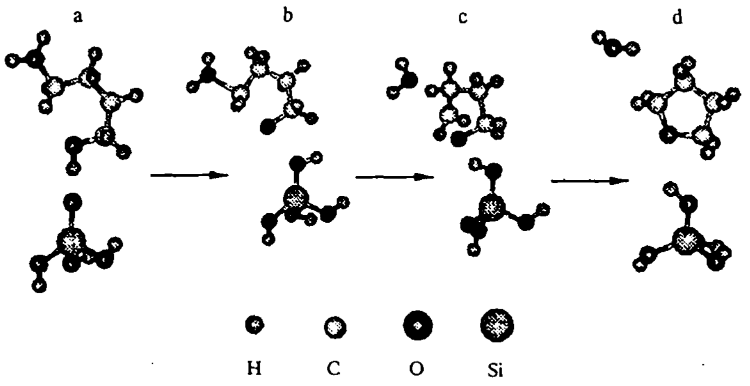


Fig. 3. Conversion of conformer (II).

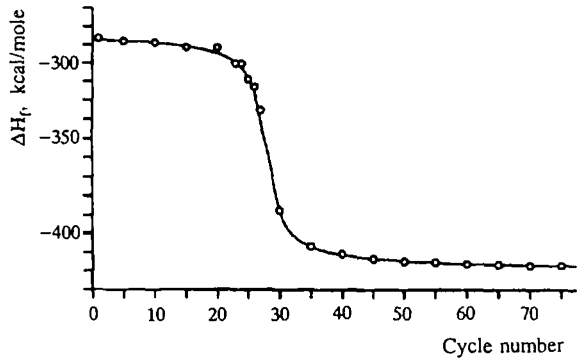


Fig. 4. Change in the heat of formation in the process of optimizing the 1,4-butanediol–active center system.

We note that the formation of 3-buten-1-ol was established on dehydrating 1,4-butanediol in the presence of a tricalcium phosphate catalyst [12].

EXPERIMENTAL

Experiments were carried out in a microcatalysis apparatus in impulse chromatographic mode at 245-300°C. Catalysts used were silica gel from Acros with a pore diameter of 60 Å, silica gel L from Chemapol (mesh size 0.035-0.07 mm), and kieselguhr (mesh size 0.25-1.00 mm, S_{sp} 5.7 m^2/g). The catalyst (15-37 mg) was placed in a steel reactor (1.2 × 3 cm) on a fiberglass support. The GLC analysis of the reaction products was carried out on a column (2.5 m × 3 mm) with 10% OV-101 + 2.5% Reoplex on chromosorb WHP as stationary phase using temperature programming from 50-150°C. The evaporator temperature was 270°C. Argon flow rate was 60 ml/min.

The quantum chemical calculations were carried out by the semiempirical AM1 method according to the MOPAC 5.0 program [13] with full optimization of geometric parameters of all structures using the algorithm of Broiden–Fletcher–Goldfarb–Shanno [14]. The key term FLEPO was used to obtain data on the change of geometric structures with time of the optimization process in the calculations. A set of values was obtained in this way characterizing the geometry of the system of each of 96 optimization cycles effected by the program. To visualize the reaction studied these values were converted into XYZ format ready for the animation and molecular structure program MOVIEMOL (K. Hermansson and L. Ojamae, University of Uppsala Institute of Chemistry, Report UUIC-B19-500). The LabVision set of programs was used for computer design of the initial 1,4-butanediol molecule and the catalyst cluster [15]. Protonation of 1,4-butanediol was simulated with H^+ ion directed to the oxygen atom of a hydroxyl group along the C–O bond of a C–O–H fragment. The distance between the oxygen atom and the H^+ ion was 5 Å in the initial state. The heat of the reaction was calculated as the difference of the heat of formation of the final system, including the reaction products and the catalyst cluster $Si(OH)_4$, and the sum of the heats of formation of 1,4-butanediol and the basic center, which was modeled with a $Si(OH)_3O^-$ cluster similarly to [16, 17].

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