

Transformation of 4-hydroxybutanal over porcelain

Ludmila Leite^{*}, Antons Lebedevs, Vladislav Stonkus, Mendel Fleisher

Latvian Institute of Organic Synthesis, 21 Aizkraukles Str., LV-1006 Riga, Latvia

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Abstract

The transformation of 4-hydroxybutanal (4-HB) in the presence of pretreated porcelain (molar ratio $\text{SiO}_2:\text{Al}_2\text{O}_3 = 6:1$) as catalyst has been investigated in a micropulse reactor at 230–300°C in a gas phase. The main reaction of the alcohol was cyclodehydration resulting in 2,3-dihydrofuran (2,3-DHF) formation. Under the conditions studied the significant irreversible adsorption of 4-HB on porcelain is observed, amounting to 1.1×10^{20} molecules/g at 240°C. The experiments with the mixture of 4-HB and 1,4-butanediol (1,4-BD) indicate that the dehydration reaction of these compounds is of a competitive character. The presence of 4-HB essentially diminishes the 1,4-BD conversion. A theoretical description of 4-HB cyclodehydration and its tautomeric cyclic form at the solid–gas interface is under discussion. The reaction mechanism has been proposed on the basis of the quantum chemical calculations. The conversion of 4-HB and its cyclic form 2-hydroxytetrahydrofuran (2-HTHF) can be interpreted by assuming the concerted mechanisms. It is suggested that the Brønsted acidic and basic $\text{Si}(\text{OH})_3\text{O}^-$ sites take part in the reactions. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

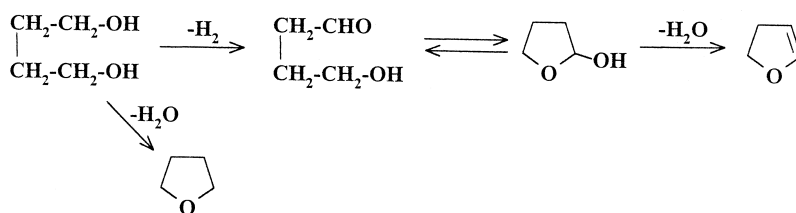
The catalytic conversion of 4-hydroxybutanal (4-HB) into 2,3-dihydrofuran (2,3-DHF) is an intermediate stage in the industrial production of the anticancer medicine Ftorafur [1]. 4-HB is obtained by dehydrogenation of 1,4-butanediol (1,4-BD) over Co/porcelain catalyst and then converts into 2,3-DHF without isolation.

In the presence of bifunctional catalyst transformation of 1,4-BD includes parallel reactions involving two cyclodehydration processes (Scheme 1). The dehydration of 1,4-BD as a side reaction decreases the selectivity to 4-HB

as well as to 2,3-DHF. The dehydration of both alcohols 4-HB and 1,4-BD occurs via the oxonium complexes formed on the Brønsted acid sites of the surface, and the competition for acid sites is possible.

Some mechanisms of alcohols cyclodehydration are discussed in the literature [2,3]. It is assumed that Lewis acids form a donor–acceptor bond with one of the OH groups of diol and induce the synchronous elimination of water and cyclization. In accordance with the other version the formation of tetrahydrofuran (THF) takes place consequently via diol adsorption on Brønsted active site, protonation of one of the OH groups, loss of water molecule accompanied by the carbenium ion formation and then

^{*} Corresponding author



Scheme 1. The conversion of 1,4-BD.

cyclization. The suggestion in relation to the carbenium ion was made on the basis of experimental investigations on monoalcohols. A mechanism for 1,4-BD conversion in the presence of porcelain and CrZSM-5 catalysts including the formation of a cyclic intermediate was also suggested [1,4]. The data for the 4-HB cyclodehydration mechanism are absent. In the present work studies of 4-HB and 1,4-BD alcohols reactions in conjunction with quantum chemical calculations are used to define some of the catalytic properties of porcelain and to elucidate the nature of catalytic sites which take part in such transformations.

2. Experimental

2.1. Materials

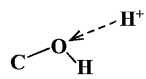
4-HB was synthesized with a purity of 98% by a modification of the method described in Ref. [5]. 1,4-BD studied was a commercial product with a purity of at least 97%. Porcelain was ($\text{SiO}_2:\text{Al}_2\text{O}_3 = 7:3$) purchased from Jensen porcelain-house (Latvia). After calcination in air at 950°C for 6 h, the porcelain was treated with hot concentrated HCl and washed with distilled water to pH 6. After such processing the $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio was 6:1. The XPS method showed that the binding energies of Si and Al are similar to those in the pure oxides (Si2p 103.3 and Al2p 74.7 eV) [1]. The Si:Al ratio of catalyst surface was found to be 2.6 by the XPS method. BET surface area was $74 \text{ m}^2/\text{g}$, pore volume 0.4 ml/g .

2.2. Methods

The experiments were carried out in vapour phase at 230 to 300°C using the microcatalytic technique. Porcelain (0.05 g) of < 0.5 mesh size was used as catalysts, the pulse size $0.5 \mu\text{l}$, the flow rate of carrier gas argon was 60 ml/min . A stainless steel reaction tube ($1.2 \times 3 \text{ cm}$) was filled with the catalyst supported by a layer of glass-fibre. The alcohols were injected into an evaporator (270°C). GLC analysis was performed using a column ($2.5 \text{ m} \times 3 \text{ mm}$) packed with 10% OV-101 + 2.5% Reoplex on Chromosorb WHP at 50 – 150°C . Chemical analysis was carried out on a RF-510 Hitachi atomic absorption spectrometer. XPS measurements were performed on a VG Scientific ESCA-3 spectrometer using $\text{Al K}\alpha_{1,2}$ radiation (1486.6 eV) from an X-ray source operating at 13 kV and 10 mA . Binding energies were referenced to the C1s peak at 284.8 eV .

Quantum chemical calculations were carried out by means of semi-empirical method AM1 using program MOPAC 5.0 [6]. Geometric parameters of all structures considered were exposed to a full optimization (Broyden–Fletcher–Goldfarb–Shanno algorithm). To obtain the data on the changes in geometry during the optimization process, calculations were performed using a keyword FLEPO. Thus, in accordance with the number of optimization cycles, realized by the program, we have obtained a set of consistent values of the system geometry. These data from MOPAC output files were converted to multi-structure XYZ files. Post processing animation was carried out with 4D-

chemical viewer/analyser ReView [7]. The computerized design of the starting molecules was performed using the LabVision Software package [8]. The protonation reaction was simulated by H^+ ion directed to the atom O along the C–O bond of the alcanol molecule fragment



The start distance between the oxygen atom and the H^+ ion was 5 Å. The proton affinity values were calculated as difference between the total energy of a molecule and its protonated form. The heat of reactions was calculated as difference between the heat formation of the final system including the reaction product and the sum of heat formation of a reagent and a catalyst cluster. The basic sites were modelled by a $Si(OH)_3O^-$ cluster similar to Refs. [9,10].

3. Results and discussion

The main reaction occurred with the alcanols 4-HB and 1,4-BD over porcelain was cyclodehydration resulting in 2,3-DHF and THF formation, respectively. The yields of both cyclization products at 230°C over the HCl-treated porcelain was 97–100%.

Under the conditions studied, significant irreversible adsorption of 4-HB on porcelain is observed, which amounts to 1.1×10^{20} molecules/g at 240°C. The irreversible adsorption of 1,4-BD is negligible. The experiments

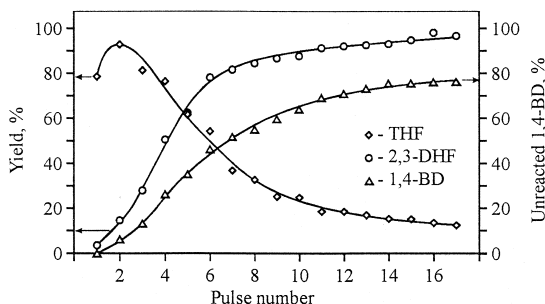


Fig. 1. Conversion of 4-HB and 1,4-BD simultaneously injected in reactor over porcelain at 240°C.

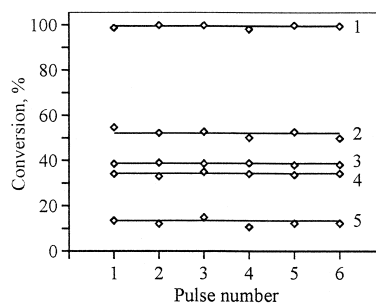


Fig. 2. Conversion of 1,4-BD over porcelain at 240°C. (1) Fresh catalyst; (2) catalyst deactivated by 4-HB at 240°C after heating at 270°C for 0.5 h; (3) catalyst deactivated by 4-HB at 240°C after heating at 300°C for 0.5 h; (4) catalyst deactivated hydroxybutanal at 240°C; (5) conversion of 1,4-BD in the presence of 4-HB over deactivated catalyst.

with the mixture of 4-HB and 1,4-BD indicate that the dehydration reaction is of a competitive character (Fig. 1).

A simultaneous injection into the reactor of both 4-HB and 1,4-BD induces a gradual increase in the 2,3-DHF yield and a decrease in the THF formation. Apparently, 4-HB essentially diminishes the 1,4-BD conversion due to the irreversible blocking of the active sites. The greater the 4-HB adsorption, the less is the 1,4-BD conversion. The increase of surface covering with 4-HB molecules decreases the selectivity to THF too (from 90 to 60%). The activity of the porcelain surface pre-deactivated by 4-HB in the 1,4-BD conversion decreases by three times in relation to the fresh catalyst (Fig. 2, curves 1, 4). In the presence of 4-HB the conversion of 1,4-BD diminishes even more (curve 5).

It may mean that the surface complexes of 1,4-BD converted into THF are formed on the surface centers active for 4-HB irreversible adsorption. A 0.5-h heat treatment of porcelain (previously worked up with 4-HB at 240°C) at 270°C in argon carrier results in a 1.5-fold increase of 1,4-BD conversion (curve 2). The subsequent heat treatment of the catalyst results in decreasing of activation effect (curve 3).

The impregnation of porcelain with NaOH (approximately 1.5×10^{20} molecules/g) leads to the 4- to 5-fold decrease of 1,4-BD conver-

sion. The conversion of 4-HB on such sample of a catalyst decreases at 230°C by only 5%.

It was been established that the cyclodehydration of 1,4-BD with heteropolyacids in liquid phase proceeds much slowly in the presence of water [11]. It can be suggested that the reaction retards due to the interaction of water molecules with the surface Brönsted sites. The effect of water in the 4-HB and 1,4-BD conversion in the gas phase over porcelain has been examined. It has been found that in our case water in the ratio 1,4-BD:H₂O = 4:1–1:4 does not change the conversion rate of the alcohols studied.

3.1. Mechanism

Similar to the mechanism suggested for monoalcohol and diols [2,3,12], it can be assumed that the dehydration reaction of 4-HB and 1,4-BD follows an oxonium-ion mechanism. The widely known supposition that the dehydration reaction of alcohols in the presence of SiO₂ (the main part of our catalyst) are realized over Brönsted acidic sites [13] has been used in our calculations.

In accordance with the quantum chemical calculations by AM1 method, 4-HB (when protonated on the hydroxyl group) is characterized by the lower value of the proton affinity than 1,4-BD (5.261 and 5.452 eV, respectively). Hence, the competition for proton containing active sites is more advantageous for the second substrate. The protonation of alcohols weakens selectively the C–O bond of C–OH₂⁺ group in 4-HB molecule to a lower degree than that in 1,4-BD molecule (bond order 0.749 and 0.819, respectively). The calculated values of 4-HB and 1,4-BD protonation heat show that the formation of the surface complexes is exothermic. The weakening of bonds in the protonated molecules allows to make a conclusion that 4-HB and 1,4-BD adsorbed on the acid centers are activated for the dehydration reaction. The visualization of the full geometry optimization process demonstrates the migration of the protonated 4-HB to a basic site and its orientation in such a mode which leads to the elimination of the water molecule and the surface complex $\text{—O—CH}_2\text{CH}_2\text{CH}_2\text{CHO}$ formation (Fig. 3a,b). For example, such transformation is observed if

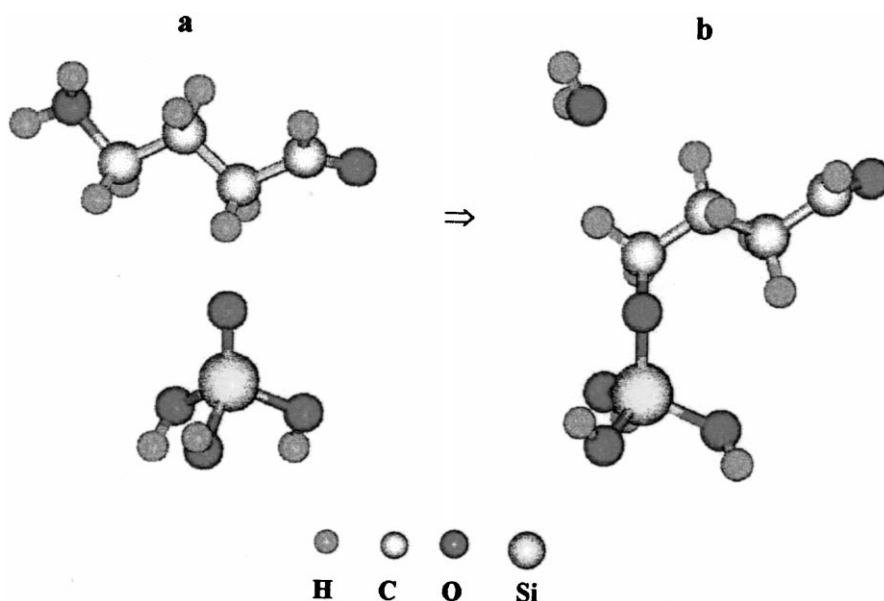


Fig. 3. The transformation of protonated 4-HB over the catalyst basic site.

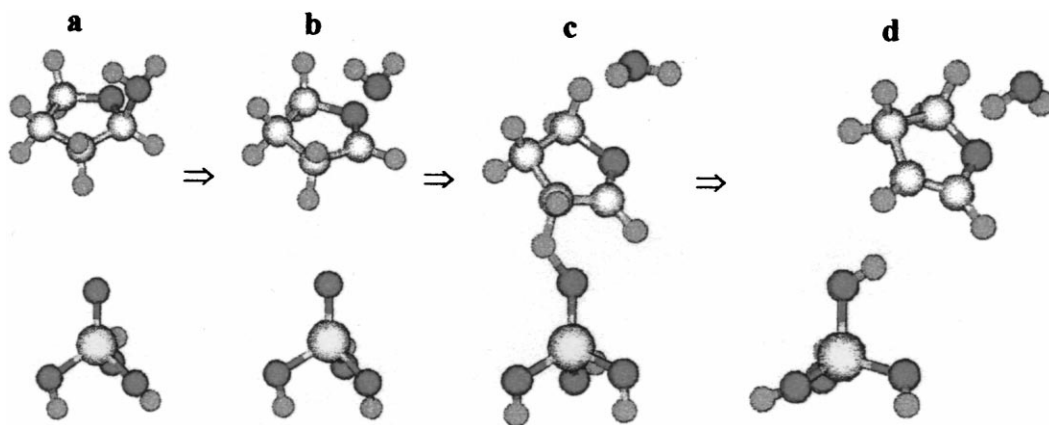


Fig. 4. The conversion of protonated 2-HTHF into 2,3-DHF over the catalyst basic site (for designation of atoms, see Fig. 3).

the initial distances between the basic center in cluster $\text{Si}(\text{OH})_3\text{O}^-$ and C2, C3, C4 atoms are 2.67, 3.79 and 3.69 Å (Fig. 3a). In this case the direction of the $\text{Si}-\text{O}^-$ bond coincides with that one of the $\text{H}-\text{C3}-\text{H}$ angle bisectrix. The reaction heat accounts for -186.290 kcal/mol. The length of the $\text{O}-\text{C4}$ and $\text{O}-\text{Si}$ bonds of the complex are 1.401 and 1.735 Å. Apparently, the alkoxide formation causes the catalyst deactivation in relation to 1,4-BD conversion.

The formation of highly reactive surface alkoxide species $\text{Si}-\text{O}-\text{C}_4\text{H}_9$ was established by authors [14] who studied the dehydration of *n*-butanol on amorphous aluminosilicate. The surface alkoxide was an intermediate in *n*-butanol conversion to butene and ether. In contrast to the butoxide species the complex formed from 4-HB is probably inactive and takes no part in the formation of the products.

4-HB is also known to have a ring form and exists as 2-hydroxytetrahydrofuran (2-HTHF) [15]. Apparently, this form participates in the 2,3-DHF formation. According to the quantum chemical calculations, this process may involve some interesting steps shown in Fig. 4.

The initial distances between the basic center and the *trans*-H atom (in relation to the OH group) of the CH_2 group in position 3 of the protonated 2-HTHF is 3.238 Å (Fig. 4a). The approach of 2-HTHF to the basic site at a

distance of 2.530 Å induces the C3–H bond weakening (the bond length changes from 1.123 to 1.139 Å) and causes the loss of water (Fig. 4b). Then the formation of the intermediate unstable complex with the length of C3–H and H–O (in cluster with the basic site) bonds making up 1.299 Å (this distance is longer than normal C–H bond) and 1.290 Å, respectively, follows (Fig. 4c). After the cleavage of bond C3–H appear 2,3-DHF and the surface OH group (Fig. 4d). The character of the change of calculating reaction system heat formation during the optimization (in the case of the 2-HTHF) shows that the conversion stages mentioned above occur without an activation barrier in the presence of a catalyst (Fig. 5).

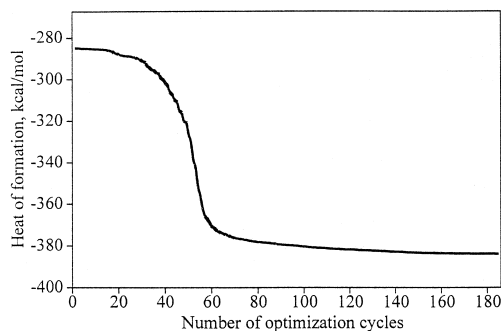


Fig. 5. The dependence of the 2,3-DHF heat formation on the number of optimization cycles.

Thus, the transformation process of the protonated 2-HTHF is actually realized via the concert mechanism. The reaction heat is -149.95 kcal/mol. Thus, the formation of a strong bounded surface complex of 4-HB is much easier than the conversion into 2,3-DHF.

4. Conclusions

4-HB transforms over porcelain into 2,3-DHF almost quantitatively at 230–300°C. A strong inhibition of 1,4-BD conversion by 4-HB is observed due to its irreversible adsorption on porcelain. The formation of 2,3-DHF and THF occurs on different active centers. The catalyst intrinsic basic sites appear to be responsible for the irreversible adsorption of 4-HB and for the transformation of 1,4-BD into THF.

Different mechanisms for the two 4-HB tautomeric forms transformation on porcelain containing clusters with Brønsted acidic and basic $\text{Si}(\text{OH})_3\text{O}^-$ sites have been considered on the basis of quantum chemical calculations. The linear 4-HB form gives inactive surface alkoxide species. The dehydration of 2-HTHF results in the 2,3-DHF formation and can be interpreted by assuming the concert mechanisms. The easiest process is a strong surface complex formation, 2,3-DHF being markedly less favourable. Apparently, clusters $\text{Si}(\text{OH})_3\text{O}^-$ take part both in the irreversible adsorption of 4-HB and in the 2-HTHF transformation to 2,3-DHF.

Acknowledgements

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