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TAUTOMERISM AND VAPOR-PHASE TRANSFORMATIONS OF 2-HYDROXYTETRAHYDROFURAN

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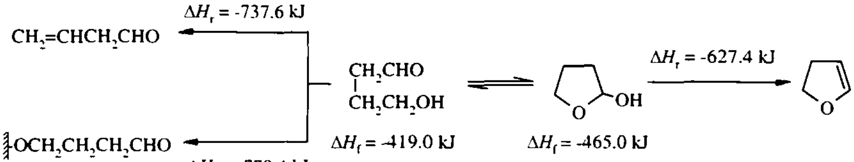
The relative stability of 2-hydroxytetrahydrofuran and the tautomeric 4-hydroxybutanal was determined by the semi-empirical AM1 method. It was concluded that the cyclic tautomer predominates in the gas phase at 25°C. Vapor-phase dehydration of 2-hydroxytetrahydrofuran in the presence of porcelain and silica gel L leads to a quantitative yield of 2,3-dihydrofuran.

Keywords: 2-hydroxytetrahydrofuran, 4-hydroxybutanal, 2,3-dihydrofuran, tautomerism, dehydration, AM1 method, concerted mechanism.

A characteristic feature of the ring–chain tautomerism of 4-hydroxybutanal (**1**) and 2-hydroxytetrahydrofuran (**2**) in solution is the prevalence of the cyclic isomer [1, 2].



1 **2** **3**

According to the data from the UV spectra, a solution in 75% dioxane at 25°C contains 88.6% of isomer **2**. We observed a similar ratio of the cyclic and linear isomers (86:14) in the absence of a solvent when the IR spectra were used to analyze the mixture.

In order to determine the position of the ring–chain tautomeric equilibrium in the gas phase we calculated the heats of formation of compounds **1** and **2** by the AM1 method, which in the opinion of the authors of [3], is preferable for this purpose. On the basis of a comparison of the obtained values (see the scheme) it was concluded that the cyclic form should also be more stable in the gas phase at room temperature. At the same time increase in temperature (>120°C) leads to weakening of the signal of the semi-acetal proton and simultaneous magnification of the carbonyl proton, indicating a shift of the equilibrium toward the aldehyde [4]. Thus, at high temperatures, where the entropy factor has a fairly high value, the equilibrium may be shifted toward the isomer whose heat of formation is lower.

We investigated the transformation of the cyclic isomer **2** in the vapor-gas phase in the presence of a series of dehydrating catalysts, including porcelain containing SiO_2 and Al_2O_3 in a ratio of 12:1 at 230-270°C (Table 1). It was found that in the presence of porcelain calcinated at 950°C and treated with hydrochloric acid and also silica gel L compound **2** is converted almost completely into 2,3-dihydrofuran (**3**); a high yield of compound **3** was obtained in the presence of kieselguhr. Increase in the temperature of the heat treatment of the porcelain to 1050°C

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leads to a decrease in the specific surface area from 18 to 12 m^2/g [5] and also to a decrease in the degree of conversion and the yield of the reaction product. If the porcelain is used without activation by acid the selectivity with respect to compound **3** does not exceed 91% on account of the formation of γ-butyrolactone as side product. Pretreatment of the porcelain with sodium hydroxide solution significantly reduces the degree of conversion of the initial compound **2** and the yield of the dehydration product **3**.

It should be noted that the yield of the desired product in the patented method for the production of dihydrofuran **3** by dehydration of the isomer **2** in the liquid phase at 35-58°C in the presence of $K_2S_2O_7$ or catalysts containing Co, Ni, and Fe does not exceed 30% [6].

Quantum-chemical calculations showed that the dehydration of the cyclic isomer **2** with the formation of dihydrofuran **3** can take place by protonation of the OH group (according to [3], the surface Brönsted acid centers of the silica gel can serve as a source of protons) followed by dehydration on the basic centers, modelled by the cluster $(HO)_3SiO^-$. Evidence for the participation of the acid centers in the reaction can be obtained from the decrease in the activity of the porcelain as a result of treatment with sodium hydroxide, which blocks these centers. At the same time the acid centers take part in the strong adsorption of the molecules of compound **1**, which is not observed before treatment of the porcelain with the acid. The decrease in the acidity of the surface after such treatment is demonstrated by the increase in the degree of conversion of 2-propanol from 4 to 100%.

The dehydration of compound **2** is an intermediate stage in the synthesis of dihydrofuran **3** from 1,4-butanediol in the presence of deposited cobalt catalysts, including the bifunctional Co/porcelain catalyst [5, 7-9]. The first stage of the reaction is dehydration of the 1,4-butanediol at the reduced cobalt and the formation of the linear isomer **1**, which then either isomerizes to the cyclic isomer **2** or is dehydrated with the formation of buten-3-al. In addition, it was established experimentally that aldehyde **1** takes part in the formation of strongly adsorbed alkoxyl complexes on the surface of the support [10]. In contrast to the surface alkoxides of other alcohols, such as butanol and ethanol [11, 12], in this case the surface complex is not an intermediate but a dead-end form, which combines the most active Brönsted acid centers and blocks the basic centers. To judge from the calculated heats of reaction, the last two types of transformation of aldehyde **1** must be energetically more favorable than the dehydration of the cyclic isomer **2**. In fact, it was shown by the pulse microcatalytic method that the first pulses of the aldehyde are transformed into surface complexes. Only after coverage of the active centers capable of taking part in the irreversible adsorption does isomerization occur, and compound **3** appears in the reaction products. The low yield of the unsaturated aldehyde (2-3%) may be due to the unfavorable mutual arrangement of the active centers on the surface of the catalyst.

The form of the irreversible adsorption of compound **1** was also confirmed by the IR spectral data. After the reaction the spectrum of the porcelain contains an absorption band at 1680 cm^{-1}, which is absent in the spectrum of the fresh porcelain and may be due to the vibrations of the carbonyl group of the adsorbed aldehyde (Fig. 1).

TABLE 1. The Catalytic Transformation of the Cyclic Isomer **2** in the Vapor-gas Phase

Catalyst	Temperature, °C		Conversion, %	Yield of 2,3-dihydrofuran, %
	catalyst calcination	reaction		
Porcelain	950	240	98	91
	1050	240	94	92
	950*	240	100	98
	950*²	230	87	78
	950	250	87	76
	950	270	90	82
Silica gel L 40/100	—	245	100	99
Kieselguhr	—	245	98	93

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*Treated with conc. HCl at 100°C.

*² Treated with NaOH solution at 100°C.

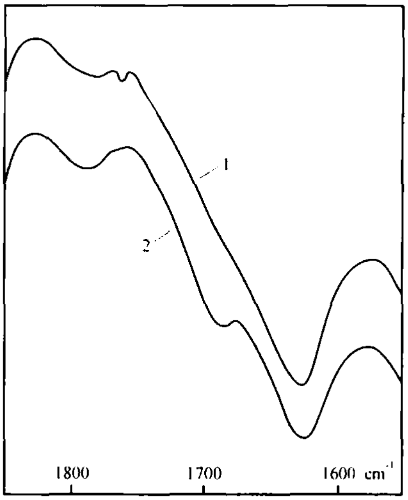
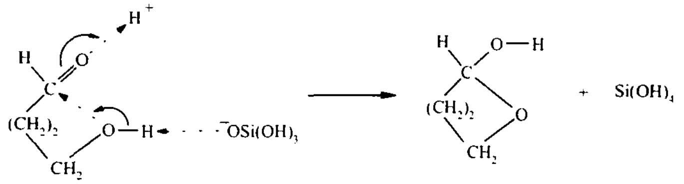


Fig. 1. A fragment of the IR spectra of porcelain:
1) before the dehydration of 2-hydroxytetrahydrofuran; 2) after the reaction.

As a result of theoretical investigations we established that the transformations of the linear isomer **1** in the presence of catalysts containing SiO_2 are regioselective and depend on the direction of attack on the basic center. The reaction with the C(1) atom of the protonated molecule **1** gives rise to the formation of the alkoxide, whereas attack by the basic center at the H atom attached to C(2) can lead to the formation of the unsaturated aldehyde [10].

The mechanism of formation and opening of lactols was studied for the case of the mutarotation of monosaccharides [13]. It was established that the closure of the ring can take place in the presence of a protic solvent and base by a concerted mechanism. In so far as the surface of the heterogeneous catalyst (porcelain) contains proton-donating and basic centers, by analogy with monosaccharides the mechanism of the cyclization of the linear isomer **1** under the conditions of heterogeneous catalyst can be represented in the following way:



EXPERIMENTAL

The IR spectra were obtained on a Perkin-Elmers 580B spectrometer. The standard for quantitative determination of the content of the linear form of the tautomer in the mixture was 3-methylbutanal. The ^1H NMR spectra were recorded on a Varian Mercury-200BB spectrometer with HMDS as internal standard. Porcelain from the Riga firm Jesena Porcelans, the characteristics of which were given in [5], was used as catalyst.

The transformations of compound **2** were studied in the vapor-gas phase at 230-300°C on microcatalytic apparatus with a reactor in the form of a steel tube (1.2 × 3 cm), filled with the catalyst (0.05 g) and glass fiber. The initial compound **2** (0.5 μl) was introduced into an evaporator heated to 270°C. The analysis of the reaction mixtures by GLC was conducted on a Chrom-5 chromatograph with a column (2.5 m × 3 mm) filled with 10% OV-101 + 2.5% Reoplex on Chromosorb WHP with a flame-ionization detector. The carrier gas (nitrogen) flow rate was 60 ml/min. The temperature regime was: 0-2 min at 50°C, 2-7 min at 150°C. The retention times of the reaction products and the initial compounds were: 50 sec (2,3-dihydrofuran); 2 min 20 sec (buten-3-al); 4 min (2-hydroxytetrahydrofuran).

The relative stability of the tautomers **1** and **2** was evaluated by comparing their heats of formation, calculated by the semi-empirical AM1 method [14]. The heats of reaction were calculated from the difference between the heats of formation of the reagents and the reaction products [10]. The suggestion about the nature of the acid and base centers of the surface of the catalyst taking part in the transformations of the tautomers **1** and **2** was made on the basis of the published data [12, 15, 16]. The change in the acidity of the catalyst surface as the result of chemical treatment was characterized by the constants of the dehydration of 2-propanol as indicator reaction [17].

2-Hydroxytetrahydrofuran (2). To a mixture of dihydrofuran **3** (15 ml, 14 g, 0.2 mol) and water (30 ml) at room temperature we added dropwise a mixture of concentrated hydrochloric acid (1.2 ml) and water (30 ml). The reaction mass was stirred for 5 min and cooled to room temperature. Sodium carbonate was added to saturation, and the mixture was extracted with chloroform (5 × 15 ml). The extract was evaporated and dried with magnesium sulfate, and the residue was distilled. We obtained 5.6 ml of a mixture of the isomers **1** and **2** (6.1 g, 35%); bp 39.5-40°C/3.2 mm Hg. Published data [2]: bp 57.5-58°C/9 mm Hg. The purity was 96% (GLC). IR spectrum, ν, cm^{-1}: 1725 (C=O), 2960, 3400 (OH). ^{1}H NMR spectrum ($CDCl_3$), ppm: 5.50 (1H, s, 2-H); 4.10-3.70 (2H, m, 5-H_2); 3.68 (1H, s, OH); 2.1-1.6 (4H, m, 3-H_2 + 4-H_2). The spectrum also contained signals for the linear form **1**, ppm: 9.78 (s, CHO); 2.54 (td, $\underline{CH_2}CHO$). The other signals of compound **1** are overlapped by the more intense signals of compound **2**. The intensity ratio of the signals of the linear and cyclic forms **1**:**2** is 1:20.

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