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SELF-OSCILLATING REACTION IN THE FURAN SERIES

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*It was found for the first time that the acid hydrolysis of 2,5-dimethylfuran in water–ethanol solutions has self-oscillating character. Oscillations in the concentrations of the two products 2,5-hexanedione and an unidentified compound **X** were detected by GLC. The ranges of hydrochloric acid and ethanol concentrations in which these oscillations appear were determined. It is suggested that the formation of compound **X** results from tautomeric transformations of 2,5-hexanedione under the reaction conditions. Quantum-chemical calculations showed that the possible tautomers are formed with equal probability.*

Keywords: 2,5-dimethylfuran, tautomers, self-oscillating reaction, acid hydrolysis.

During the development of a method for the production of thiophenes and selenophenes by the recyclization of furans in water–ethanol media under the conditions of acid catalysis it was shown that the reaction takes place in two directions, one of which includes a stage involving the formation of a diketone, i.e., hydrolysis. Kinetic investigations of the hydrolysis of 2,5-dimethylfuran (**1**) in 50% ethanol under the influence of HCl revealed the formation of 2,5-hexanedione (**2**) and an unidentified compound **X**. During the reaction the ratio of the concentrations of the products varied with some degree of periodicity, i.e., as it accumulated one product changed into the other, and these transformations were self-oscillating in nature [1, 2].

Study of the behavior of furan compounds in aqueous and water–alcohol media under the conditions of acid catalysis is of great theoretical and practical interest in so far as oscillating chemical reactions take place in various types of processes that determine the vital activity of living organisms [3], while furan derivatives are physiologically active substances.

In the present work in order to determine the boundary conditions for the appearance of the above-mentioned transformations the kinetics of the hydrolysis of dimethylfuran **1** in 50% aqueous ethanol with various hydrochloric acid concentrations (1.5, 2.0, 3.0, 3.5 N) were investigated by GLC. The results of the experiments are presented in Fig. 1. As seen, the fluctuations in the contents of the dione **2** and compound **X** in the reaction medium are observed at HCl concentrations (c) of 1.5-2.0 M. At $c = 3$ M both products are formed, but the ratio of their amounts in the reaction medium does not change with time.

The experiments in 60 and 80% ethanol at HCl concentrations of 2.0 and 2.5 N (the dimethylfuran is poorly soluble in the 40% alcohol) showed that in 80% alcohol at the indicated acid concentrations only the hexanedione **2** is formed, while in 60% ethanol the concentrations of compound **2** and **X** oscillate in both cases (Fig. 2).

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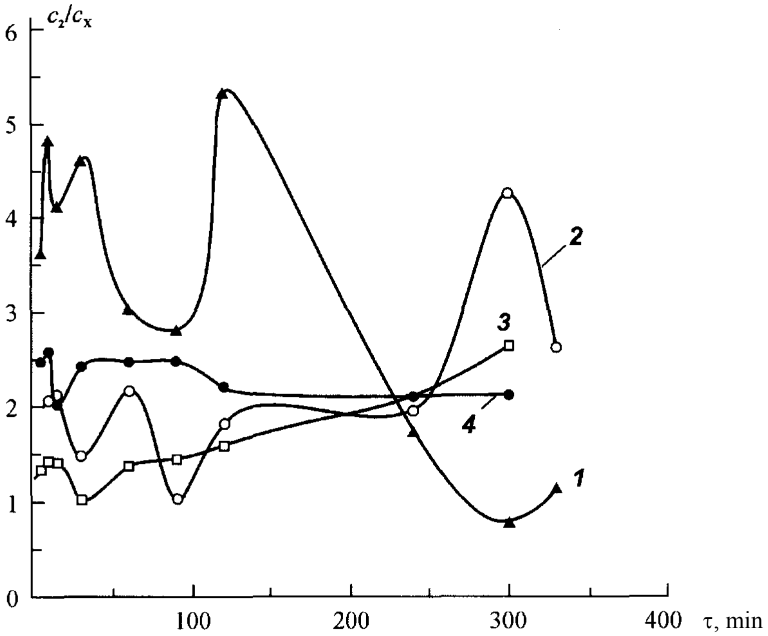


Fig. 1. The kinetic curves for the hydrolysis of dimethylfuran **1** in 1.5 (1), 2.0 (2), 3.0 (3), and 3.5 N (4) solutions of HCl in 50% aqueous ethanol; c_2 is the concentration of hexanedione **2**; c_X is the concentration of compound **X**.

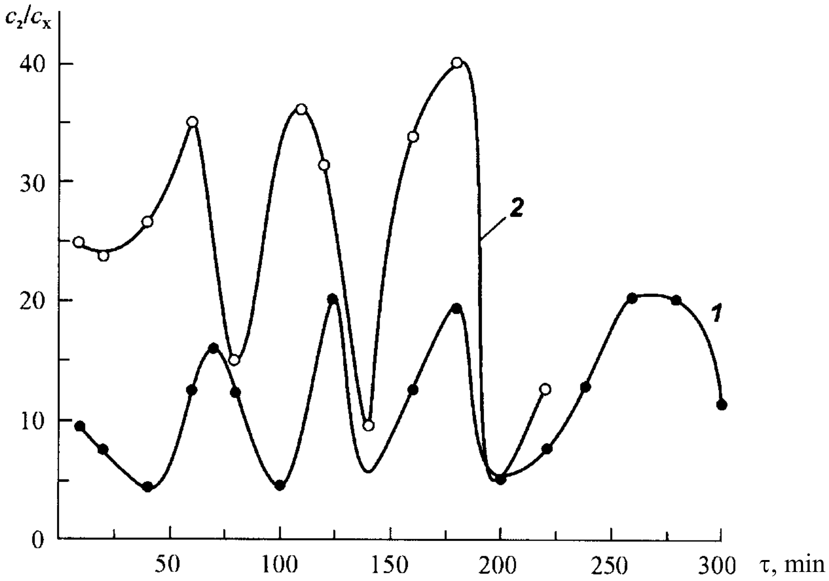


Fig. 2. The kinetic curves for the hydrolysis of dimethylfuran **1** in 2.0 (1) and 2.5 N (2) solutions of HCl in 60% aqueous ethanol.

The oscillations in the concentrations of the hexanedione **2** and compound **X** are in our opinion explained by the formation of dimethylfuran **1** from the reaction products and its subsequent hydrolysis. This was confirmed by the following experiment: The dione **2** was kept in a 2 N solution of hydrochloric acid in 50%

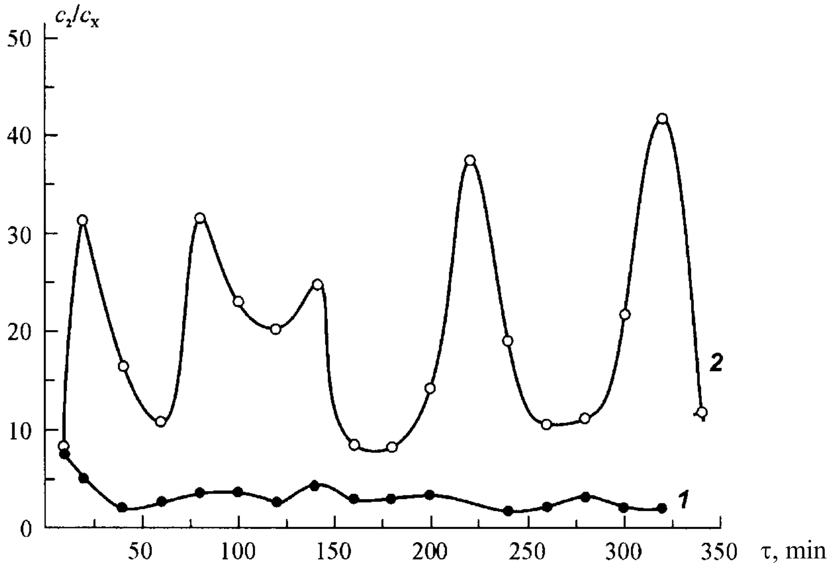


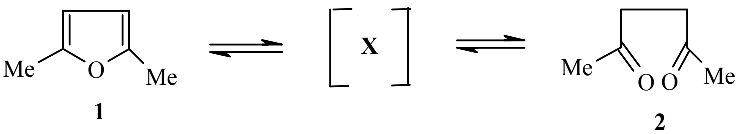
Fig. 3. The kinetic curves for the protolytic reaction: 1) Hexanedione **2** in a 2.0 N solution of hydrochloric acid in 50% aqueous ethanol; 2) after the addition of dimethylfuran **1** to the reaction mixture.

ethanol, compound **X** was found, and its content oscillated with a very small amplitude (Fig. 3, curve 1). The addition of dimethylfuran **1** to the reaction mixture led to a significant increase in the amplitude of oscillation (Fig. 3, curve 2).

Thus, we had found that the hydrolysis of dimethylfuran **1** in acidic water–ethanol media is an autocatalytic reaction.

During attempts to establish the structure of compound **X** it was assumed that it may represent a ketal or semiketal of hexanedione **2**, since hydrolysis was conducted in a water–ethanol medium [1]. However, it was not possible to isolate compound **X** from the reaction mixture during distillation of an ether extract; it was converted into hexanedione **2**. According to GLC, the same dione and a small amount of the product **X** (~8-10%) were mainly formed during hydrolysis of the dimethylfuran **1** in a 2 N aqueous solution of hydrochloric acid, but without oscillation in the concentrations. This made it possible to exclude the formation of a ketal or semiketal of hexanedione.

Since the hydrolysis of compound **1** includes a proton transfer stage, we assumed that the formation of compound **X** results from the appearance of keto–enol tautomerism in the hexanedione **2**, while the substance **X** is its tautomer. The following scheme of mutual transformations was proposed: The hexanedione **2** is formed from the dimethylfuran **1** in the acidic medium; this can exist in several tautomeric forms, which are transformed spontaneously from one to the other. In turn, the enol form of the dione **2** is readily transformed into dimethylfuran **1**, which again undergoes hydrolysis:



In order to confirm the presented scheme we recorded the electronic spectra of compounds **1** and **2** in 50 and 96% ethanol, water, and hexane and also the electronic spectra of the reaction mixture after various time intervals (Fig. 4). Dimethylfuran **1** has absorption bands at 216 (in 50% ethanol), 218 (in 96% ethanol), 216 (in

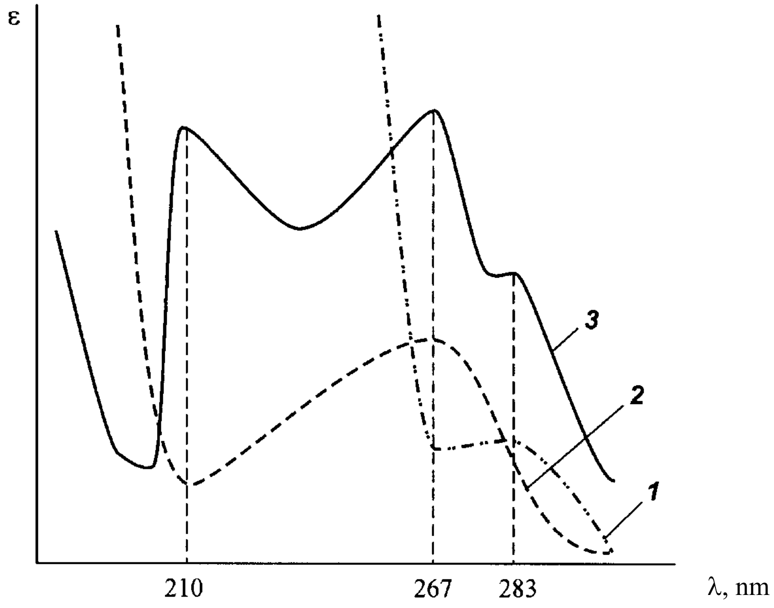


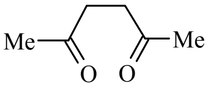
Fig. 4. The electronic spectra of dimethylfuran **1** (1) and hexanedione **2** (2) in 50% ethanol and of the reaction mixture (3) 40 min after the beginning of the reaction.

water), and 224 (in hexane). Hexanedione **2** absorbs at 264 nm in water and water–ethanol solution, at 280 nm in hexane, and at 266 nm in 96% ethanol. The absorption band of dimethylfuran **1** (216-224 nm) is characterized by high intensity and corresponds to the permitted π–π* transition. The absorption band of hexanedione **2** at 264-280 nm has low intensity and belongs to the *n*–π* transition localized in the carbonyl group. The type of electronic transition here (*n*–π*) is confirmed by the hypsochromic shift of the absorption band with increase in the polarity of the solvent.

In the water–ethanol solution the absorption band of the substrate at 218 nm becomes weaker with time but does not disappear throughout the whole period of the observations (5 h). A weak band for the *n*–π* transition appears at 288 nm and probably corresponds to the carbonyl chromophore. The spectra indicate that hydrolysis of the dimethylfuran **1** with the formation of the saturated diketone **2** in the water–ethanol medium takes place with great dilution with the solvent and even in the absence of the acid. If the reaction is carried out in the cuvette (50% ethanol, 2 N HCl) three absorption bands are recorded in the reaction mixture: One of them (216 nm) corresponds to the dimethylfuran **1**, the second (264 nm) to the hexanedione **2**, and the third (283 nm) to the unknown product. According to data in [4], this last band may correspond to 2-hydroxy-2,5-dimethyl-3-dihydrofuran. Thus, the data from electronic spectroscopy indicate indirectly that the hexanedione **2** undergoes tautomeric transformations under the investigated reaction conditions.

In order to identify possible tautomers and also to compare acetone and its enol quantum-chemical calculations of the standard entropies, the heats of formation, the Gibbs energies of formation, and the dipole moments of the electronic structures of hexanedione **2** and its tautomers **2A**-**F** were undertaken (Table 1).

According to the calculations, hexanedione **2** is the most thermodynamically stable. Its ability to undergo enolization is greater than that of the monoketone acetone. The *cis*- and *trans*-ketoenols **2A**-**C**, like their isomer 2-hydroxy-2,5-dimethyl-2,3-dihydrofuran **2D**, are energetically equivalent, which does not contradict their possible existence in the reaction medium. The formation of the dienol tautomers of hexanedione **2E**,**F** is less likely than monoenolization. The formation of the dienols is energetically comparable with the enolization of acetone.



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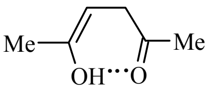
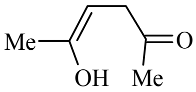
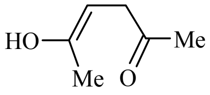


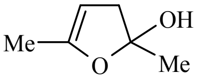
cis-**2A**



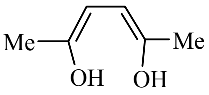
cis-**2B**



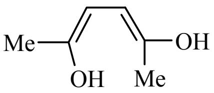
trans-**2C**



2D



cis-**2E**



trans-**2F**

TABLE 1. The Dipole Moments (μ), Standard Heats of Formation (ΔH_j), Entropies (S), and Gibbs Energies of Formation (ΔG_f) (the M3 Method)

Compound	μ, D	ΔH_f, kcal/mol	S, kcal/mol·K	ΔG_f, kcal/mol
2	2.45	-96.59	99.92	-62.81
2A	3.06	-89.11	94.37	-53.68
2B	2.15	-88.93	95.24	-53.60
2C	2.49	-88.48	96.23	-53.76
2D	1.24	-88.44	88.64	-51.30
2E	2.52	-84.62	96.28	-49.76
2F	0.026	-83.16	98.26	-48.89
Acetone	2.78	-53.32	70.93	-38.03
Acetone enol	1.95	-38.78	70.88	-23.48

On the basis of our investigations the scheme of the oscillating reaction may have the following form:

$$\mathbf{1} \longleftrightarrow \left[\mathbf{2E} \longleftrightarrow \mathbf{2A} \longleftrightarrow \mathbf{2D}\right] \longleftrightarrow \mathbf{2}$$

We studied the oscillating processes in the protolytic hydrolysis of dimethylfuran **1**. The oscillations in the concentrations of the reaction products (hexanedione **2** and compound **X**) only occur under specific reaction conditions (at HCl concentrations of 1.5-2.5 M in 50 and 60% ethanol). It is not possible to isolate the unknown product and establish its structure by the usual chemical methods. The electronic spectra indicate the possible formation of tautomers of hexanedione **2**, but the effect requires further investigation, which we will be undertaking.

EXPERIMENTAL

The reactions were monitored and qualitative and quantitative analysis of the reaction mixtures was performed by GLC and UV spectroscopy. Gas-liquid chromatography was conducted on a Tsvet-101 chromatograph with a flame-ionization detector on columns (1 m × 3 mm and 3 m × 3 mm) with 15% Apiezon L on Chromaton N-AW: Thermostat temperature 100°C, carrier gas (helium) flow rate 2 l/h.

The UV spectra were recorded on an HP 8452A spectrometer in the region of 200-300 nm at steps $x = 2$ nm. The quantum-chemical computations were performed by the SCF LCAO MO PM3 method using MOPAC software by analogy with [5].

Compounds **1** and **2** were prepared by the usual procedures [6].

Kinetic Investigations of the Hydrolysis of 2,5-Dimethylfuran 1. General Procedure. In a 50-ml reaction vessel provided with a thermostated jacket (reaction temperature 40°C) in a vibroscope we placed dimethylfuran **1** (0.48 g, 5 mmol), *o*-xylene (0.15 g) (internal standard), and the calculated amounts of twice-distilled water, 90% ethanol, and 12 N hydrochloric acid to create alcohol concentrations of 80, 60, and 50% and acid concentrations of 3.5, 3.0, 2.5, 2.0, and 1.5 N in 20 ml of solution. At specific intervals 1-ml samples were taken from the reaction mixture, concentrated potassium hydroxide (sodium hydroxide) (2 ml) was added to each, and the mixture was extracted with ether (1 ml). The contents of the components in the mixture were determined by GLC with an internal standard.

Hydrolysis of 2,5-Dimethylfuran 1. Hydrolysis was conducted in a 2 N solution of hydrochloric acid according to the procedure described above (dimethylfuran **1** (0.48 g, 5 mmol) in 20 ml of solution). Quantitative control of the reaction was realized by GLC.

2,5-Hexanedione (2). The compound was kept in a 2 N aqueous solution of hydrochloric acid in 50% ethanol under conditions similar to those described above, using hexanedione **2** (0.57 g, 5 mmol). After 2 h dimethylfuran **1** (0.48 g, 5 mmol) was added to the solution (Fig. 3).

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