FURAN ACETAL COMPOUNDS

I. STUDY OF THE KINETICS OF HYDROLYSIS OF SOME SUBSTITUTED FURAN 1,3-DIOXANES

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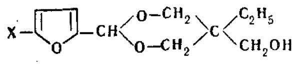
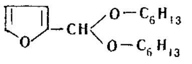
It is shown that furan 1,3-dioxanes are considerably more stable than analogous systems with acyclic structures in hydrolysis reactions. The process is described by a first-order kinetic equation and is a reversible monomolecular reaction. A correlation was observed between the rate constants for the hydrolysis of α'-substituted furan acetals and the magnitude of the solvatochromic effect and the Brown σ^+ constants.

In recent years interest has grown in cyclic systems of the 1,3-dioxane type [1]. However, the state of investigations of such compounds of the furan series is not reflected in the well-known monographs [2, 3], and the literature does not contain data on the hydrolysis of these compounds.

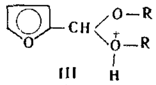
This study set out to explain the dependence between the rate of hydrolysis of furan acetals and their structures. The subjects of the investigations were the cyclic acetal of 2-furyl-5-ethyl-5-hydroxymethyl-1,3-dioxane (I, X = H), its derivatives with various substituents in the 5-position of the furan ring, and a model acyclic compound – furfurylidenedihexylacetal (II).



I

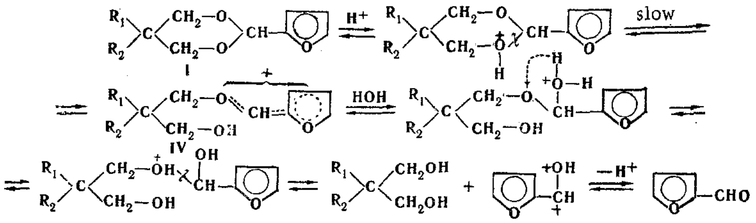


II



III

The proposed mechanism for the hydrolysis of furan 1,3-dioxanes (I) can be presented as follows in the light of the theory of acid catalysis [3, 4]:



In the hydrolysis of II, the determining step is apparently the formation of intermediate carbonium ion III, which is in agreement with the data in [4]. In contrast to this, the slowest step in the hydrolysis of I is cleavage of the dioxane ring to form carbonium ion IV.

In the literature the hydrolysis reactions of such systems are treated as reversible and irreversible [5].

An investigation of the kinetic curves (Fig. 1, Curves 1, 2, and 3) makes it possible to establish that the hydrolysis of I proceeds reversibly. Under similar conditions, product II was cleaved almost completely and instantaneously. The kinetics of the hydrolytic cleavage of II (Curves 4 and 5) could be observed only

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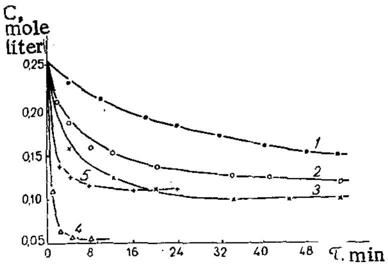

Fig. 1. Kinetic curves for the cleavage of 2-furyl-5-ethyl-5-hydroxymethyl-1,3-dioxane (1-3) in 0.5 N H_2SO_4: 1) at 40 deg; 2) at 50 deg; 3) at 60 deg; and of furfurylidenedihexylacetal (4,5) in 0.01 N H_2SO_4: 4) at 40 deg; and 5) at 23 deg.

with a decrease in the reaction temperature and catalyst concentration (to 0.01 N). A confirmation of the reversibility of the hydrolysis is also found in a study of the kinetics of formation of furan 1,3-dioxanes from furfural derivatives and alcohols [6].

The kinetic data obtained were analyzed mathematically using the following equations:

For a reversible first-order reaction,

$$v = k_1(c_{ac} - c'_{ac}) - k_2(c_f - c'_f), \tag{1}$$

$$k_1 = k_{eq} \cdot k_2, \tag{2}$$

$$k_2 = \frac{2,3}{\tau} \lg \frac{k_{eq} c_{ac}}{k_{eq} c_{ac} - c'_{ac}(k_{eq} + 1)}; \tag{3}$$

For a reversible second-order reaction,

$$v = k'_1(c_{ac} - c'_{ac}) c_{H_2O} - k'_2(c_f - c'_f)(c_{al} - c'_{al}), \tag{4}$$

$$k'_1 = k_{eq} k'_2, \tag{5}$$

$$k'_2 = \frac{2,3}{2c_{ac}\tau\sqrt{k_{eq}}} \lg \frac{c_{ac}\sqrt{k_{eq}} - c'_{ac}(\sqrt{k_{eq}} - 1)}{c_{ac}\sqrt{k_{eq}} - c'_{ac}(\sqrt{k_{ac}} + 1)}, \tag{6}$$

where k_1 and k'_1 are the rate constants of the forward reaction; k_2 and k'_2 are the rate constants of the reverse reaction; c_{ac} is the starting acetal concentration in moles per liter; c'_{ac} is the amount of acetal converted in time τ in moles per liter; k_{eq} is the equilibrium constant calculated from Eq. (7); and c_f, c_{al}, and c^e_{ac} are the equilibrium concentrations of furfural, alcohol, and acetal in moles per liter.

$$k_{eq} = \frac{c_f \cdot c_{al}}{c_{ac}^{e}}. \tag{7}$$

In deriving the equations we assumed that the initial concentration of the hydrolysis products was zero.

It is apparent from the data in Table 1 that the rate constant for the reversible first-order reaction is constant, so that all of the subsequent calculations were accomplished from Eq. (2).

Rate constants of 0.055, 0.200, and 0.700 min^{-1}, respectively, were obtained by studying the hydrolysis of I (X = H) at various temperatures (313, 323, and 333 deg K). The experimental activation energy, calculated from the Arrhenius equation, is 25,000 cal/mole.

The reactivity of α'-substituted furan 1,3-dioxanes in hydrolysis reactions was compared with the solvatochromic shifts in their UV spectra. For this, we investigated the kinetics of the hydrolysis of I (X=H, CH_3, Br, Cl, NO_2) and also obtained the UV spectra of these compounds in water and hexane.

The correlation between the rate constant and the solvatochromic effect makes it possible to calculate the rate constants for substituted acetals I from the equation $\log k = 0.05 - 1.3 \cdot 10^{-4}\Delta\nu_{1,2}$ (r = 0.98).

The magnitude of the hydrolysis rate constant depends substantially on the nature of the substituent (Table 2) and increases in the order $CH_3 > H > Cl > Br > I > NO_2$.

TABLE 1. Kinetics of Hydrolysis of 2-Furyl-5-ethyl-5-hydroxymethyl-1,3-dioxane*

τ, min	c_{ac}, mole/liter	k_1, min^{-1}	k_1', liter · $mole^{-1}$ · min^{-1}
1	0,010	0,0537	0,110
2	0,020	0,0539	0,160
3	0,025	0,0535	0,140
4	0,030	0,0540	0,125
5	0,034	0,0535	0,110
7	0,038	0,0535	0,100
10	0,046	0,0537	0,100

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* 0.5 N H_2SO_4, 40 deg, acetal:water = 1:25, c_{ac} = 0.26 mole/liter, k_{eq} = 0.25 mole/liter.

The rate constants are also very correlated with the Brown σ^+ constants [8] (Fig. 2): $\log k = -1.26 - 2.4\sigma^+$ (r = 0.96). The dependence obtained and the sign and magnitude of the reaction constant confirm the proposed reaction mechanism.

EXPERIMENTAL

The 2-(α-furyl)-5-alkyl-5-hydroxymethyl-1,3-dioxanes and furfurylidenedihexylacetal were obtained via the method in [9]. The crystalline products were additionally purified by recrystallization from benzene-heptane, while the liquid products were purified by vacuum distillation. Dioxane was freed from peroxide,

TABLE 2. Rate Constants and Solvatochromic Shifts for α'-Substituted Furan 1,3-Dioxanes (I).

No.	Substituent X in I	k, min^{-1} (40°C)	λ_{max}, nm		$\Delta\nu_{1,2} \cdot 10^{-4}$, cm^{-1}*
			water	hexane	
1	CH_3	0,300	219,0	217,4	3,4174
2	H	0,055	217,1	215,2	3,9500
3	Cl	0,038	223,0	221,0	4,0210
4	Br	0,027	222,0	220,0	4,0950
5	I	0,010	228,0	225,6	4,5122
6	NO_2	0,00003	306,0	300,0	6,5333

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*$\Delta\nu_{1,2} = \lambda^{water}_{max} - \lambda^{hexane}_{max}$.

dried, and subjected to fractional distillation. The purity of the solvent and the absence in it of acetals were monitored from the UV spectra.

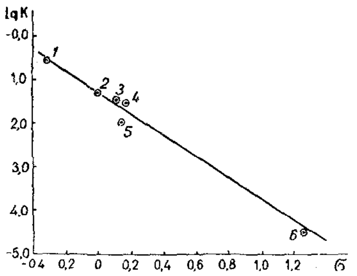

Fig. 2. Correlation of the hydrolysis rates of 2-(α-furyl)-5-alkyl-5-hydroxymethyl-1,3-dioxanes with the σ^+ substituent constants. (The numbering of the points corresponds to that in Table 2.)

Method of the Kinetic Measurements. The acetal (0.0125 mole), dissolved in 50 ml of dioxane, was placed in a thermostated three-necked flask equipped with a reflux condenser, stirrer, and thermometer; aqueous sulfuric acid solution served as the catalyst for the hydrolysis. The start of the reaction was taken as the moment of introduction of the catalyst into the solution. The light absorption of the starting acetal (216-306 nm) decreased regularly during the reaction, and absorption appeared at 270-320 nm, which is characteristic for the final product; this made it possible to measure the concentrations of both the acetal and furfural by a spectrophotometric method [7].

Compounds I were hydrolyzed under the following conditions: the acetal:water ratio was 1:25, the concentration of the starting aqueous H_2SO_4 was 0.5 N, and the temperature was 40 deg. Compounds II were hydrolyzed under similar conditions and at H_2SO_4 concentrations of 0.1 and 0.01 N and at 23 deg. In the latter case the hydrolysis rate constant of II is 0.820 min^{-1}.

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