3. The relative amount of the isomers in the mixture and the thermodynamic parameters of the equilibrium were determined.

4. The steric conditions created by the two aryl radicals in the third compound lead to a stabilization of one predominant conformer in all of the states of the compound, with a gauche orientation of the OCH_3 with respect to the P = Se bond.

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METHANOLYSIS OF 4-METHYL-1,3-DIOXANE

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The alcoholysis of 1,3-dioxanes is used to synthesize 1,3-diols, alcohol ethers, and dienic hydrocarbons [1]. The present paper is devoted to a study of the products and kinetics of the indicated reaction on the example of the methanolysis of 4-methyl-1,3-dioxane in the presence of H_2SO_4.

EXPERIMENTAL METHOD

4-Methyl-1,3-dioxane (MD), synthesized as described in [2], was repeatedly distilled over Na, bp 114.5°; n_D^{20} 1.4165; d_4^{20} 0.9747. The methanol (MN) was purified as described in [3].

The methanolysis of the MD was run by heating a mixture of 29.3 g of MD, 193.0 g of MN, and 26.7 g of H_2SO_4 at 60-65°C for 3.5 h. The mixture was cooled, neutralized with dry NH_3, and filtered. Atmospheric distillation through a precise fractionation column (8 theoretical plates) gave 158.0 g of MN, 6.1 g of MD, and 16.2 g (93.4%) of methylal (MA), bp 42.2°; n_D^{20} 1.3530; d_4^{20} 0.8610. Vacuum-distillation of the residue through a microcolumn gave 16.0 g (93.2%) of 1,3-butanediol (BD) [4] (bp 92-93° (3 mm); n_D^{20} 1.4408; d_4^{20} 1.0039) and 2.0 g (6.6%) of 3-methyl-4,6-dioxa-1-heptanol (MDH) (bp 67-69° (5 mm); n_D^{20} 1.4220; d_4^{20} 0.9862).

The reaction rate was studied in thermostatted 3-ml glass ampuls. At the end of experiment the ampuls were cooled rapidly to −18°, and the mixture was neutralized with dry NH_3 and then analyzed for the amount of MD and reaction products by GLC (flame-ionization detector, 13% nitrile-siloxane rubber deposited on INZ-600, 50-120°, and carrier gas = helium). Based on the data of the control experiments, treatment of the reaction mixture with ammonia does not affect the analysis results.

DISCUSSION OF RESULTS

The main reaction products of MD with methanol are MA and BD. The indicated products are formed in parallel in practically the same yields; in view of the last fact, we analyzed for only MD and MA in all of the kinetic experiments. The typical kinetic curves for the consumption of MD and the accumulation of MA are

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TABLE 1. Dependence of K and k_1 on the Reaction Conditions

T., °C	$[H_2SO_4]$	$[MD]_0$	$[MN]_0$	$[MD]_e$	$[MN]_e$	$[MA]_e$	$K \cdot 10^3$, liter/mole	$k_1 \cdot 10^5$, liter/mole·sec
	mole/liter							
70,0	0,91	0,58	21,10	0,08	20,10	0,50	7,7	3,44
70,0	0,91	0,96	20,07	0,22	18,59	0,74	7,2	3,83
70,0	0,91	1,53	18,60	0,52	16,57	1,01	7,2	4,00
60,0	0,20	0,96	21,00	0,25	19,58	0,71	5,3	0,25
60,0	0,46	0,96	20,70	0,25	19,28	0,71	5,4	0,56
60,0	0,91	0,96	20,07	0,26	18,67	0,70	5,4	1,20
50,0	0,91	0,96	20,07	0,29	18,70	0,67	4,4	0,40
40,0	0,91	0,96	20,07	0,34	18,83	0,62	3,2	0,10

Remarks. $[MD]_0$, $[MN]_0$, $[MD]_e$, $[MN]_e$, and $[MA]_e$ are respectively the initial and equilibrium concentrations of the compounds.

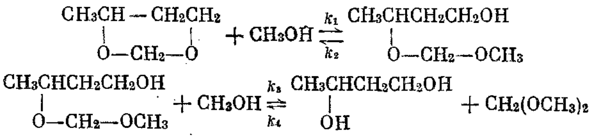
given in Fig. 1, from which it can be seen that the methanolysis of MD is a reversible reaction. To measure the empirical equilibrium constants K of the process the experiments were run until the reaction stopped completely.

As the result of determining K at various temperatures (Table 1) it was found that

$$K = \frac{[BD]_e[MA]_e}{[MD]_e[MN]_e^2} = 0{,}6 \cdot 10^2 \cdot \exp\,(-6100/RT)\ \text{liter/mole}.$$

Together with MA and BD, 3-methyl-4,6-dioxa-1-heptanol is formed in the methanolysis of MD, which apparently is the primary reaction product. The assumption that hemiformals and their derivatives are formed as intermediate products in the hydrolysis, etherification, and methanolysis of 1,3-dioxanes was expressed previously [5-7]. In the present paper this assumption was confirmed experimentally for the first time for the case of methanolysis.

In view of the above said the sequence in the formation of the methanolysis products of MD can be described by the following scheme.



In harmony with the scheme the rate for the accumulation of MA is described by the expression:

$$W = \frac{d\,[MA]}{d\tau} = k_3\,[MDH\,]\,[MN] - k_4\,[MA]^2$$

Since the MN concentration remains essentially unchanged during experiment, $[MN] \approx [MN]_0$, while $[MDH] \ll [MA]$, [BD] (due to the high reactivity of MDH toward MN).

$$[MDH\,] \approx \frac{k_1\,[MD]\ [MN]_0 + k_4[MA]^2}{k_2 + k_3\,[MN\,]_0}$$

Consequently

$$\frac{d\,[MA]}{d\tau} \approx \frac{k_1k_3\ [MD]\ [MN]_0^2 - k_2k_4\,[MA]^2}{k_2 + k_3\,[MN]_0}$$

After integration and the appropriate transformations we obtain

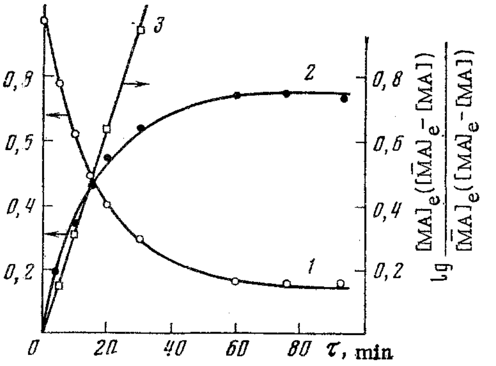


Fig. 1. Kinetic curves for consumption of MD (1) and accumulation of MA (2); 3) anamorphosis of 2 in the coordinates: $\lg\{[MA]_e([MA]_e - [MA])/\overline{[MA]}_e([MA]_e - [MA])\}$ vs. time (70°, $[H_2SO_4]$ 0.91 mole/liter, $[MD]_0$ 0.96 mole/liter).

$$2{,}3\ \lg\frac{[\mathrm{MA}]_e([\overline{\mathrm{MA}}]_e-[\mathrm{MA}])}{[\overline{\mathrm{MA}}]_e([\mathrm{MA}]_e-[\mathrm{MA}])}\approx\frac{[\mathrm{MA}]_e-[\overline{\mathrm{MA}}]_e}{K[\mathrm{MN}]_0}k_1\tau$$

where [MA] and $[\mathrm{MA}]_e$ are respectively the current and equilibrium concentration of MA, mole/liter, and $[\overline{\mathrm{MA}}]_e = -[\mathrm{MA}]_e - K[\mathrm{MN}]_0^2$.

The last equation satisfactorily describes the accumulation rate of MA (see Fig. 1) and makes it possible to determine k_1 (see Table 1).

From the data in Table 1 it follows that: $W \sim [\mathrm{MD}]_0$, $\lg k_1 = -4.87 + 1.04 \lg [H_2SO_4]$, and $k_1 = 6.9 \cdot 10^{12} \cdot \exp(-27{,}000/RT)$.

CONCLUSIONS

1. A study was made of the products and rate of methanolysis of 4-methyl-1,3-dioxane in the presence of H_2SO_4.

2. The methanolysis of 4-methyl-1,3-dioxane proceeds with the successive cleavage of the C_2-O_1 and C_2-O_3 bonds of the ring; 3-methyl-4,6-dioxa-1-heptanol is formed as an intermediate reaction product.

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ACETOXY DERIVATIVES OF trans-1,2-DISILYLETHYLENE AND THEIR HYDROLYSIS

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Alkoxysilanes when reacted with carboxylic acids and their anhydrides are converted to the corresponding acyloxy derivatives [1, 2]. This reaction when applied to ethynylalkoxysilanes and $(CH_3CO)_2O$ is a convenient method for the preparation of ethynylacetoxysilanes [3]. The reaction of $(CH_3CO)_2O$ with the mono- and dimethoxy-trans-1,2-disilylethylenes (I), (II), and (VII)-(IX), catalyzed by p-toluenesulfonic acid was studied in the present paper.

It was established that these compounds, similar to the alkoxysilanes, easily exchange the CH_3O group for the CH_3COO group when treated with $(CH_3CO)_2O$, with conversion in high yield (60-90%) to the mono- and diacetoxy-trans-1,2-disilylethylenes (III), (IV), (X)-(XII).

Acetoxysilylethylenes (III), (IV), (X)-(XII) are very sensitive to water and even at ~20°C are hydrolyzed by it to silanols (V), (VI), (XIII)-(XV).

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