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KINETICS OF CHLOROMETHYLATION OF BENZO-1,4-DIOXANE

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UDC 547.841:541.127

The chloromethylation of benzo-1,4-dioxane in acetic acid in presence of $SnCl_4$, $SbCl_3$, $ZnCl_2$, and $SbCl_5$ catalysts was investigated. The activation energy of the process was found to be 19.6 kcal/mole. The reaction is zero order in chloride ion and first order in the Hammett acidity function. In excess HCl the reaction is described by a second-order equation. The relative activities of the methyl chlorides in the chloromethylation of benzo-1,4-dioxane were determined.

Benzo-1,4-dioxane derivatives, which are of interest owing to their pharmacological properties [1, 2], can be synthesized by haloalkylation. Chloromethylation, to which a good deal of study has been devoted in the case of aromatic hydrocarbons, has been the subject of relatively little study in the case of compounds of the benzo-1,4-dioxane series [3-8], and it has not yet been evaluated quantitatively. In our communication we present kinetic data on the chloromethylation of benzo-1,4-dioxane in acetic acid in the presence of zinc, tin(IV), antimony(III), and antimony(V) at 50-75°C. A study of the kinetic principles of this reaction confirms its acid-catalytic mechanism

$$CH_2O + H^+ \rightleftharpoons {}^+CH_2OH$$

$${}^+CH_2OH + ArH \longrightarrow ArCH_2OH + H^+$$

$$ArCH_2OH + HCl \rightleftharpoons ArCH_2Cl + H_2O$$

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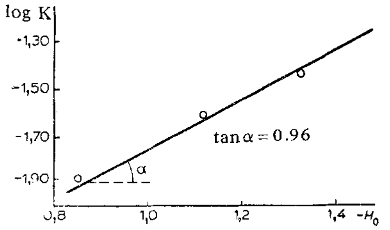

Fig. 1

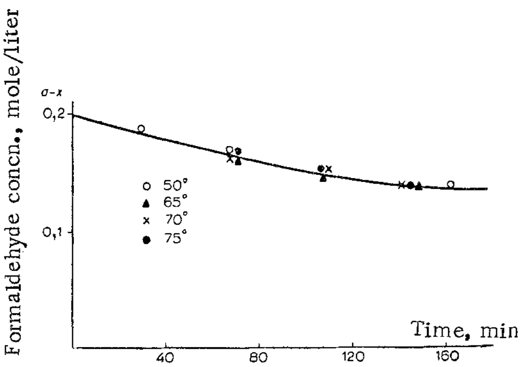

Fig. 2

Fig. 1. Effect of acidity function H_0 on the rate of chloromethylation at 50°C.

Fig. 2. Transformation of the kinetic curves with respect to formaldehyde.

TABLE 1. Effect of the Addition of Chloride Ions on the Rate of Chloromethylation at 65°C

No.	Initial conc., mole/liter					
	CH_2O 0.2, benzo-1,4-dioxane 0.2, H_2SO_4 0.6			CH_2O 0.2, benzo-1,4-dioxane 0.2, H_2SO_4 0.6, LiCl 0.2		
	time, τ, min	instantaneous formaldehyde conc., a-x, mole/liter	rate constant, K, liters-mole^{-1}-min^{-1}	time, τ, min	instantaneous formaldehyde conc., a-x, mole/liter	rate constant, K, liters-mole^{-1}-min^{-1}
1	10	0,145	0,189	11,5	0,140	0,186
2	21,5	0,105	0,190	22	0,112	0,178
3	33,5	0,090	0,182	33,5	0,090	0,182

and shows that the reaction rate is described by the third-order equation

$$W = K_0[H_0][CH_2O][ArH],$$

proposed for the chloromethylation of aromatic hydrocarbons [9], where H_0 is the Hammett acidity function, and CH_2O and ArH are the concentrations of formaldehyde and the aromatic hydrocarbon, respectively. The rate-determining step is the second step in the process.

In the case of a virtually constant value of the acidity function, which is achieved by the use of excess HCl, this equation is converted to a second-order equation, and the rate constant for identical initial concentrations of formaldehyde and benzo-1,4-dioxane has the form

$$K = \frac{x}{\tau \cdot a(a-x)},$$

where K is the rate constant in liters per mole per minute, τ is the time in minutes, *a* is the initial concentration of formaldehyde and benzo-1,4-dioxane in moles per liter, and x is the conversion of formaldehyde in moles per liter.

It was established that the reaction is zero-order in chloride ion (Table 1) and first-order in acidity function H_0 (Table 2 and Fig. 1).

The change in the acidity as a function of the temperature complicates the determination of the parameters of the Arrhenius equation [10]. The activation energy of the reaction was therefore determined by means of the transformation coefficients [11] using the kinetic curves of the change in the formaldehyde concentration with time (Table 3).

The curve obtained at 50°C, to which the other curves were transformed, was used as the standard curve. It is seen in Fig. 2 that the curves coincide satisfactorily. The equation of the line that expresses the dependence of the logarithms of the transformation coefficients on the reciprocal of the temperature (Fig. 3) was found by the method of least squares [12]. Activation energy E determined from the slope of this line ($E = 4.57 \tan \psi$j,

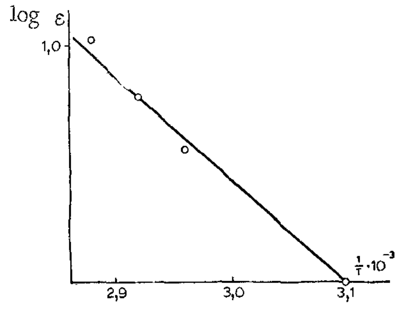

Fig. 3

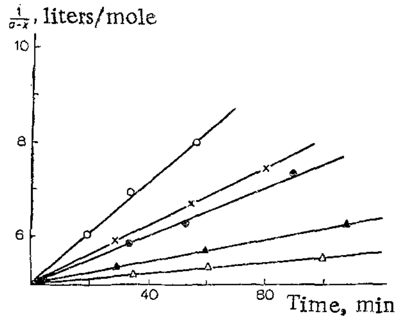

Fig. 4

Fig. 3. Dependence of the logarithms of the transformation coefficients on the reciprocal of the temperature.

Fig. 4. Dependence of the reciprocal of the instantaneous formaldehyde concentration on the time: ○) $SnCl_4$; ×) $SbCl_3$; ●) $ZnCl_2$; ▲)without a catalyst; △) $SbCl_5$.

TABLE 2. Effect of the Acidity on the Rate of Chloromethylation at 50°C

HCl conc., mole/liter*	Acidity function, $-H_0$	Time, τ, min	Instantaneous formaldehyde conc., a-x, mole/liter	Rate constant, $K\cdot10^{-2}$, liters-$mole^{-1}$-min^{-1}	Logarithm of the rate constant, K_{av}
0,6	0,86	30	0,185	1,36	−1,87
		68	0,170	1,30	
		108	0,155	1,34	
0,8	1,12	23,5	0,180	2,36	−1,62
		60	0,155	2,42	
		98	0,135	2,46	
1,0	1,33	24	0,170	3,71	−1,42
		49	0,145	3,91	
		86	0,125	3,82	

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*a = 0.2 mole/liter.

TABLE 3. Kinetic Data for the Chloromethylation of Benzo-1,4-dioxane

Temp., °C	Contact time, τ, min	Instantaneous formaldehyde concn., a-x, mole/liter	Rate constant,* $K\cdot10^{-2}$, liters-$mole^{-1}$-min^{-1}
50	30	0,185	1,36
	68	0,170	1,30
	108	0,155	1,34
	162	0,140	1,32
65	20,5	0,170	4,3
	31,0	0,155	4,7
	56,0	0,130	4,8
	70,0	0,120	4,7
70	5,0	0,180	11,1
	17,0	0,145	11,2
	28,0	0,125	10,2
	43,0	0,105	10,6
75	3,00	0,170	29,4
	7,50	0,140	29,4
	10,0	0,130	28,2
	25,0	0,090	30,0

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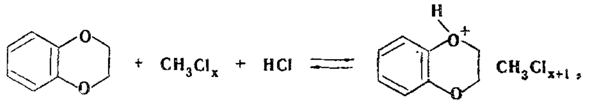
*Initial concentrations: a = 0.2 mole/liter, b = 0.2 mole/liter, and [HCl] = 0.6 mole/liter.

where j is the ratio of the scale along the axis of abscissas to the scale along the axis of ordinates) is 19.6 kcal/mole.

With respect to their activities, the metal chlorides used as catalysts in the chloromethylation of benzo-1,4-dioxane are arranged in the order $SnCl_4 > SbCl_3 \simeq ZnCl_2 > SbCl_5$ (Fig. 4).

Tin(IV), antimony(III), and zinc chlorides accelerate chloromethylation, while antimony(V) slows it down. This difference can be explained, in our opinion, as follows. On the one hand, the chlorides presented above tend to form complex acids of the $H_2[SnCl_4(OCOCH_3)_2]$ type, which are weaker than mineral acids [13], and this should intensify protonation of formaldehyde and increase the speed of the rate-determining step of the reaction. In this connection, one might have expected the highest rate in the presence of $SbCl_5$ as the strongest Lewis acid in the investigated series of chlorides. On the other hand, the chlorides that we used probably form benzo-1,4-dioxanates via these pathways:



similar to the complexes obtained in the reaction of dioxane with aluminum, arsenic, and antimony chlorides [14, 15]. Thus, whereas visible changes are not observed when $ZnCl_2$ is added to benzo-1,4-dioxane, $SbCl_3$ gives rise to slight coloration, $SnCl_4$ gives rise to coloration and warming, and $SbCl_5$ forms a dark-violet precipitate that has limited solubility in acetic acid. From the data obtained it may be concluded that antimony pentachloride benzo-1,4-dioxanate has the highest stability, and this decreases the effective concentrations of the reactants and, consequently, lowers the rate of chloromethylation. The formation of unstable benzo-1,4-dioxanates of other chlorides does not make a contribution to slowing down the reaction rate.

EXPERIMENTAL

Benzo-1,4-dioxane, with bp 216°C and n_D^{20} 1.5526, was synthesized from pyrocatechol and dibromoethane [16].

Monochloromethylbenzo-1,4-dioxane, with bp 126-128°C (3 mm), was obtained by the following method. A 0.5-liter flask was charged with 180 ml of CH_3COOH, a solution of 6 g (0.2 mole) of CH_2O in concentrated HCl, and 27.2 g (0.2 mole) of benzo-1,4-dioxane. Hydrogen chloride was passed through the reaction mixture with stirring at 50°C. The contact time was 20 min. Neutralization, drying, and distillation gave 16.2 g (45%) of monochloromethylbenzo-1,4-dioxane, 12.9 g of recovered benzo-1,4-dioxane, and 1.4 g of residue.

Thus the selectivity of the reaction was 85%. After treatment of the reaction products with a methanol solution of NaOH, chromatographic analysis confirmed the presence of only benzo-1,4-dioxane, its methoxymethyl derivative, and 1% impurities [with an LKhM-8MD chromatograph, Apiezon L on Chromaton, a column temperature of 220°C, a 3-m long column, a detector current of 80 mA, and a carrier-gas (hydrogen) flow rate of 35 ml/min. The high selectivity of the reaction made it possible to estimate its rate from the rate of conversion of formaldehyde [9].

Kinetic data for the reaction were obtained by using a 250-ml flask equipped with a stirrer, a mercury seal, and a reflux condenser.

A 30-ml sample of a solution of 2 moles of HCl in 1 liter of CH_3COOH, 10 ml of a solution of 2 moles of CH_2O in 1 liter of water, and 40 ml of CH_3COOH (50 ml of CH_3COOH if metal chlorides were not used), were poured into the flask, and 10 ml of a solution of 2 moles of benzo-1,4-dioxane in 1 liter of CH_3COOH and 10 ml of a solution of 1 mole of the metal chloride in 1 liter were measured out into a test tube. The flask and the test tube were thermostatted for 30 min at the selected temperature (±0.5°C). The contents of the test tube were poured into the flask, and the reaction starting time was noted. For analysis, 2-ml samples were selected and introduced into KOH solution taken in a small excess. The formaldehyde concentration was determined by means of a microburet with a solution of sodium sulfate [17]. Glacial acetic acid, reagent-grade formalin, and anhydrous chemically pure-grade metal chlorides were used. The values of the acidity function for solutions of HCl and H_2SO_4 in 90% CH_3COOH were taken from [9].

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SYNTHESIS AND SPECTRAL-LUMINESCENCE PROPERTIES OF 4,4'-DI(2-OXAZOLYL)-STILBENES AND 4,4'-DI(2-OXAZOLYL)TOLANS

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A new method is proposed for the synthesis of 4,4'-di(2-oxazolyl)stilbenes and 4,4'-di(2-oxazolyl)tolans by condensation of oxazolyl-substituted benzyl bromides or benzal dibromides under the influence of strong bases (KOH, potassium tert-butoxide) in dipolar aprotic solvents [dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)]. The synthesized compounds luminesce intensely over the spectral range 386-492 nm.

Compounds of the stilbene and tolan series that contain oxazole fragments have intense luminescence in the blue region of the spectrum [1, 2]. 4,4'-Di(2-oxazolyl)stilbenes are used as optical bleaches [1]. In addition, 4,4'-di(2-oxazolyl)stilbene is known as an active substance for lasers [3]. Less study has been devoted to the difficult-to-obtain 4,4'-di(2-oxazolyl)tolans; however, there are data that indicate that they can also be used as optical bleaches [4].

At present there are no convenient methods for the preparation of dioxazolyl-substituted stilbenes and tolans, and this significantly hinders the study of their spectral-luminescence properties. The usual methods for the synthesis of 4,4'-di(2-oxazolyl)stilbenes are based on the cyclodehydration of substituted amides of stilbene-4,4'-dicarboxylic acid [1, 5]. The specific method for their preparation consists in the oxidative dimerization of 2-(p-tolyl)oxazoles [1, 6]. The synthetic methods based on the Wittig–Horner reac-

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