CATALYTIC TRANSFORMATIONS OF BENZOFURAN

IV.* VAPOR-PHASE ALKYLATION OF BENZOFURAN WITH tert-BUTYL CHLORIDE

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When benzofuran is alkylated with tert-butyl chloride in the vapor phase (190-260°C) in a flow system, the ratio of the 2- and 3-tert-butylbenzofurans formed varies from 2 : 1 to 20 : 1, depending on the acidity of the catalyst used ($ZnCl_2/Al_2O_3$), because of conversion of the 3-isomer to the 2-isomer.

We studied the alkylation of benzofuran with tert-butyl chloride at 190-260°C in a flow-type apparatus on samples of Al_2O_3 and $ZnCl_2/Al_2O_3$ of different acidity (Table 1). The chief reaction products were 2- (I) and 3-tert-butylbenzofurans (II), the ratio of which varied from 2 : 1 to 20 : 1, respectively, while isomer II always predominated in experiments at lower temperatures (60-100°) in the catalyzates in a static system [2].

The predominant formation of isomer I in experiments in the vapor phase is associated with isomerization of II to I, which occurs under the influence of catalysts with an acidic function (Table 2); reverse transformation was not observed under the investigated conditions. This sort of isomerization of alkylbenzofurans in the presence of a heterogeneous catalyst with a relatively low acidity has not been previously noted. It follows from Table 2 that the isomerization of II to I is accompanied by the formation of benzofuran and isobutylene, the amount of which increases as the temperature rises and the acidity of the catalyst increases; this apparently is evidence for intermolecular isomerization [3].

TABLE 1. Alkylation of Benzofuran with tert-Butyl Chloride (space velocity 0.15 h^{-1}, reagent ratio 1 : 1)

Catalyst	Catalyst acidity*	Temp., °C	Yield based on converted benzofuran, %		
			I	II	phenols
Al_2O_3	0,2	185	25	10	1
		200	28	12	2
		230	28	13	2
		260	30	15	5
5% $ZnCl_2/Al_2O_3$	1,0	185	28	11	21
		200	38	10	20
		230	36	6	20
		260	38	2	35
10% $ZnCl_2/Al_2O_3$	1,5	185	36	4	20
		200	42	4	25
		230	44	2	27
		260	30	2	43
20% $ZnCl_2/Al_2O_3$	3,0	185	21	1	33
		200	20	1	42
		230	15	—	60
		260	7	—	

*The number of milliequivalents of n-butylamine consumed in the titration of 1 g of catalyst is presented.

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*See [1] for communication III.

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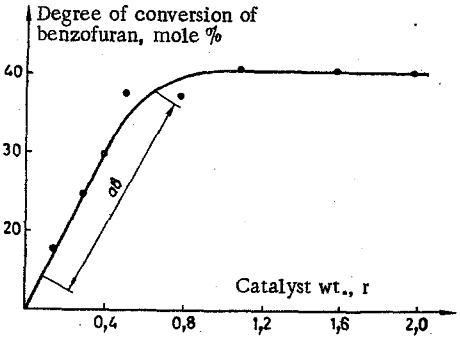


Fig. 1. Dependence of the degree of conversion of benzofuran on the amount of Al_2O_3 (space velocity 0.8 h^{-1} at 230°C).

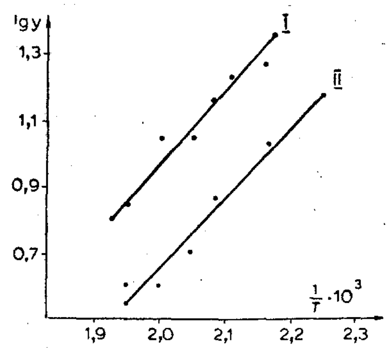


Fig. 2. Dependence of the amount of alkylation products formed on the temperature: I) 2-tert-butylbenzofuran; II) 3-tert-butylbenzofuran.

TABLE 2. Isomerization of 3-tert-Butylbenzofuran (II) (space velocity 1.15 h^{-1})

Catalyst	Temperature, °C	Composition of the liquid catalyzate, %			
		benzofuran	I	II	phenols
Al_2O_3	260	—	1	99	—
5% $ZnCl_2/Al_2O_3$	260	2	4	94	—
10% $ZnCl_2/Al_2O_3$	200	7	—	90	3
	220	11	3	83	2
	240	11	8	77	4
	260	15	13	67	5
	280	9	23	65	3
	300	20	4	73	3
	320	19	1	77	3
20% $ZnCl_2/Al_2O_3$	260	20	19	56	5

TABLE 3. Dependence of the Degree of Conversion of Benzofuran on the Temperature (space velocity 0.8 h^{-1}, γ-Al_2O_3 catalyst)

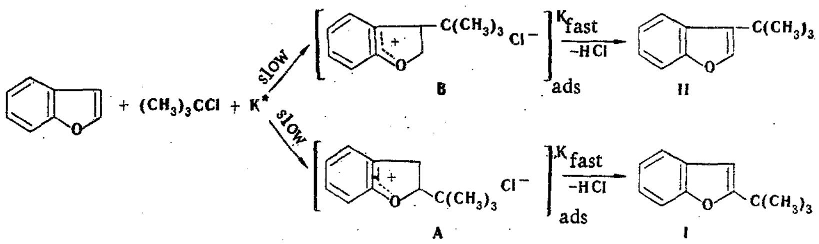
Temperature, °C	Yield, mole %		Converted benzofuran, mole %	Amount of benzofuran remaining on the catalyst, mole %
	I	II		
190	17	10	44	7
200	17	10	37	7
208	14	7	30	7
220	13	5	24	8
230	11	4	20	6
240	9	4	17	6

We studied some kinetic principles of the alkylation of benzofuran in a flow system under conditions that exclude isomerization. The experiments were carried out on γ-Al_2O_3 (0.25-0.5-mm fraction).

The experimental conditions also excluded occurrence of the reaction both in the external and internal diffusion regions. The dependence of the degree of conversion of benzofuran on the amount of catalyst is presented in Fig. 1; segment *ab* on the curve characterizes the kinetic region of the occurrence of the reaction.

The amount of converted benzofuran (in the presence of a tenfold excess of tert-butyl chloride) is independent of its concentration; a similar pattern is also observed for tert-butyl chloride, which means apparent zero-order of the reaction with respect to both benzofuran and tert-butyl chloride. The independence of the degree of conversion of benzofuran on the space velocity also confirms a zero-order reaction. This makes it possible to suppose that the slow step in the alkylation is conversion of the adsorbed complex on the catalyst.

The formation of isomers I and II is characterized by identical temperature coefficients (Fig. 2), and the step involving the formation of σ complexes A and B is apparently the rate-limiting step.



It follows from Table 3 that the degree of conversion of benzofuran in the presence of a tenfold excess of tert-butyl chloride decreases as the temperature rises.

A similar pattern was also observed with 1 : 1, 1 : 2, and 2 : 1 ratios of reacting substances. The regularities obtained are associated with suppression of alkylation due to poisoning of the active centers of the catalysts by the condensation products and inhibition by the reaction products.

EXPERIMENTAL

The isomerization was carried out in a flow system with a 1.5 ml detachable reactor in a stream of dry nitrogen. The volume of the catalyst (0.25-0.5 mm fraction) was 1 ml. The yield of catalyzate was 98-99%.

A detachable quartz reactor (80-mm long and 10 mm in diameter) was used to determine the kinetic parameters. The catalyst was an industrial sample of Al_2O_3 (0.5-0.25-mm fraction) with a surface area of 206 m^2/g, determined by the gas sorption method (with nitrogen). The aluminum oxide was calcined at 500° for 4 h and treated with 60% water (based on the weight of Al_2O_3) prior to the experiments. The catalyst was dried at 300° for 4 h. All of the experiments were carried out in a stream of nitrogen on a fresh portion of catalyst (from 0.4 to 2 g). Samples were selected after 10 min.

LITERATURE CITED

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