CATALYTIC ALKYLATION OF BENZOFURANS

II.* KINETIC PRINCIPLES OF THE ALKYLATION OF BENZOFURAN BY TERT-BUTYL CHLORIDE

É. A. Karakhanov, G. V. Drovyannikova,   UDC 547.728.1:541.128.13.127.1:542.951
and E. A. Viktorova

The kinetic characteristics of the alkylation of benzofuran by tert-butyl chloride in the presence of zinc chloride were determined. It is shown that the processes involved in the formation of 2- and 3-tert-butylbenzofurans are parallel and that the rate-limiting step of the reaction is the formation of the polarized $(CH_3)_3C^+$ ... $ZnCl_3$ complex.

As previously reported in [1], 2- and 3-tert-butylbenzofurans were the reaction products in the alkylation of benzofuran by tert-butyl chloride in the presence of $ZnCl_2$. Continuing our investigations of this re-reaction under static conditions, we have determined some kinetic parameters of the reaction. The reaction was carried out in the kinetic region, where its rate was independent of the rate of stirring.

To determine the reaction order in benzofuran, we studied the dependence of the reaction rate on the benzofuran concentration (0.75-2.0 mole/liter) at 70 deg C in the presence of a tenfold excess of tert-butyl chloride. The experimental results are presented in Table 1 and Fig. 1, from which it is apparent that the reaction is zero order with respect to benzofuran.

The reaction rate as a function of the tert-butyl chloride concentration (0.5-1.75 mole/liter) was determined for a tenfold excess of benzofuran at 60 deg. The experimental results (Table 1 and Fig. 2) demonstrate that the reaction is first-order with respect to tert-butyl chloride, as is the reaction with respect to the catalyst (Fig. 3).
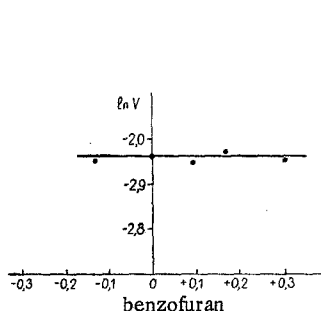
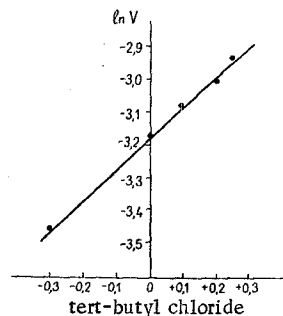

Fig. 1.   Fig. 2.

Fig. 1. Determination of the reaction order of the alkylation with respect to benzofuran (in toluene at 70 deg).

Fig. 2. Determination of the reaction order to the alkylation with respect to tert-butyl chloride (in toluene at 60 deg).

*See [1] for communication I.

TABLE 1.

TABLE 1. Determination of the Reaction Order of the Alkylation with Respect to Tert-Butyl Chloride and Benzofuran in Toluene

Temp.	Exptl. conditions	Indexes				
60	Starting tert-butyl chloride concn., mole/liter	0,5	1,0	1,25	1,5	1,75
	Reaction rate in tert-butyl chloride, mole/liter-min·10^{-4}	3,33	6,7	8,3	10,0	11,7
70	Starting benzofuran concn., mole/liter	0,75	1,0	1,25	1,5	2,0
	Reaction rate with respect to benzofuran, mole/liter-min·10^{-3}	10,8	11,1	10,1	9,9	9,9

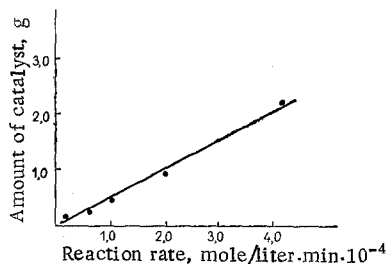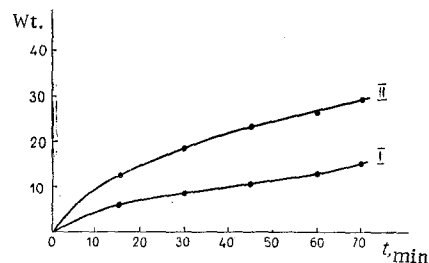Fig. 3

Fig. 4.

Fig. 3. Dependence of the rate of alkylation on the amount of $ZnCl_2$ (in toluene at 60 deg for a tert-butyl chloride concentration of 0.75 mole/liter).

Fig. 4. Dependence of the amount of alkylation products formed on the reaction time: I) 2-tert-butylbenzofuran; II) 3-tert-butylbenzofuran (at 68 deg with toluene as the solvent and a benzofuran concentration of 0.75 mole/liter).

TABLE 2. Dependence of the Rate of Alkylation on the Temperature for a Zero-Order Reaction in Toluene

| Experimental conditions	50						60						70						78					
Starting benzofuran concn., mole/liter	0,5	0,75	1,0	1,25	1,75	2,0	0,5	1,0	1,25	1,75	2,0		0,5	0,75	1,0	1,25	1,5	2,0	0,5	0,75	1,0	1,25	1,5	2,0
Rate of formation of 2-tert-butylbenzofuran, mole/liter-min·10^{-4}	1,86	1,9	1,86	1,93	1,86	1,93	3,20	3,75	3,15	3,15	3,78		11,7	11,7	11,5	11,7	15,3	11,5	17,0	20,0	17,0	26,0	26,0	23,0
Rate of formation of 3-tert-butylbenzofuran, mole/liter-min·10^{-4}	5,6	5,8	3,8	3,8	3,8	5,8	12,6	13,3	11,6	11,7	11,5		15,4	15,4	19,3	19,3	15,6	15,4	45,0	37,0	23,0	53,0	51,0	44,0

The dependence of the amount of 2- and 3-tert-butylbenzofurans formed on the reaction time is presented in Fig. 4. The trend of the curves indicates that the formation of both isomers proceeds in a parallel manner; this is confirmed by the absence of mutual isomerization of 2- and 3-tert-butylbenzofurans under the experimental conditions. The dependence of the rate of formation of 2- and 3-tert-butylbenzofurans on the temperature (50-78 deg) as the starting benzofuran concentration changes from 0.5 to 2.0 mole/liter in the presence of a tenfold excess of tert-butyl chloride in toluene is presented in Table 2.

On the basis of the results, we calculated the apparent energy of activation, which proved to be 8.7 and 8.5 kcal/mole for 2-tert-butylbenzofuran and 3-tert-butylbenzofuran, respectively. The equality of the apparent energies of activation for the formation of the alkylbenzofuran indicates that the reaction to form both isomers proceed through a single rate-limiting step.

Since the reaction is first-order with respect to tert-butyl chloride and catalyst and zero-order with respect to benzofuran, the rate-limiting step is the formation of a polarized complex:
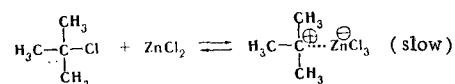
The subsequent course of the reaction can be represented as follows:
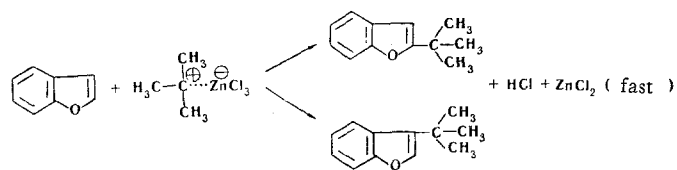
EXPERIMENTAL

The experiments were carried out at 50–78 deg in a flask thermostated at ± 0.5 deg with constant stirring under nitrogen. The stirring rate was 1000 rpm. The conditions involved in the chromatographic analysis of the catalyst and the characteristics of the reagents used are presented in [1].

LITERATURE CITED

1. É. A. Karakhanov, G. V. Drovyannikova, and E. A. Viktorova, Khim. Geterotsikl. Soedin., 156 (1971).