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Figure 1

Figure 1: Figure 1

Abstract

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KINETICS OF THE POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF BORON FLUORIDE ETHERATE

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The present work is devoted to a study of the kinetics of the polymerization of $i\mathrm{C_4H_8}$ in the presence of the complex compound of diethyl ether with boron fluoride: $(\mathrm{C_2H_5})_2\mathrm{O}\cdot\mathrm{BF_3}$. To avoid diffusion interference, the experiments were carried out in such a way that the catalyst $(\mathrm{C_2H_5})_2\mathrm{O}\cdot\mathrm{BF_3}$ was present as a thin adsorbed film on the surface of tubes made of fused quartz.

Before an experiment, the reactor with a packing of quartz tubes (free volume 0.34 l; surface area of the packing ~ 0.5 m^2) was evacuated to a pressure of $\sim 10^{-4}$-10^{-5} mm Hg. First, the required vapor pressure of ether was established in the reactor; then boron fluoride was admitted. The amount of $\mathrm{BF_3}$ admitted into the reactor was determined from its consumption from a bulb of known volume. In each experiment the equilibrium pressures of etherate ($P^r_{\mathrm{e-t}}$), boron fluoride (P^r_{BF3}), ether in the gas phase (P^r_{ef}), and the amount of etherate ($P^\ell_{\mathrm{e-t}}$) condensed on the surface were determined. For calculation of these quantities the following data were used: the equilibrium constant for dissociation of etherate in the gas phase,

$$K_p = \frac{P^r_{\mathrm{BF3}}\cdot P^r_{\mathrm{ef}}}{P^r_{\mathrm{e-t}}} = 92.5$$

(at $t = 70°$), from the data of Brown and Adams (^{1}), the value of the established total pressure (P_{sum}) in the reactor after admission of boron fluoride and ether, and the balance equations for P_{BF3} and P_{ef}.

Fig. 1. Kinetic curve (and its anamorphosis) of the polymerization of $i\mathrm{C_4H_8}$ in the presence of boron fluoride etherate. $t = 70°$. $P^2 = 74.2$; $P^2_{\mathrm{ef}} = 4.8$; $P_{i\mathrm{C4H_8}} = 52$ mm Hg; $V_{\mathrm{react}} = 0.34$ l.

Particular attention was paid to the preparation of pure reagents containing no traces of moisture. Boron fluoride was prepared and purified by a method developed by us ([2]). Diethyl ether was distilled in a rectifying column over metallic sodium and stored in flasks with sodium. Isobutylene was fractionated on a highly efficient vacuum column and dried by bubbling through a liquid Na –K alloy.

The reaction rate was expressed in terms of the decrease in the pressure of isobutylene (mm Hg per minute in a reactor of volume 1 l), referred to 1 mole of adsorbed etherate. Figure 1 presents the kinetic curve and its anamorphosis for the process of polymerization of $i\mathrm{C_4H_8}$ in the presence of $(\mathrm{C_2H_5})_2\mathrm{O}\cdot\mathrm{BF_3}$. At $t = 70^\circ$ and small $P_{i\mathrm{C4H_8}}$ (up to 100-150 mm Hg), the kinetic curves are well described by a second-order equation up to 40-50% conversion, and the rate constant K_1 determined in this way does not depend on the initial pressure of $i\mathrm{C_4H_8}$.

At $P_{i\mathrm{C4H_8}}$ from 30 to 110 mm Hg, the influence of the pressures of $\mathrm{BF_3}$ and ether in the gas phase on the catalytic activity of $(\mathrm{C_2H_5})_2\mathrm{O}\cdot\mathrm{BF_3}$ was investigated.

Ether and boron fluoride are connected by the equilibrium $\mathrm{BF_3(C_2H_5)_2O} \rightleftarrows \mathrm{BF_3} + \mathrm{(C_2H_5)_2O}$; to facilitate interpretation of the results, the experiments were carried out under such conditions that the vapor pressure of the etherate was close to or equal to saturation, i.e., at constant thermodynamic activity of the etherate. It was found that, when P_{ether} is increased from 1.8 to 72 mm Hg, the catalytic rate constant K_1 decreases by more than a factor of 40 (Fig. 2 and Table 1). Owing to the absence of data on the partial vapor pressures of $(\mathrm{C_2H_5})_2\mathrm{O}$ and $\mathrm{BF_3}$ over solutions of $(\mathrm{C_2H_5})_2\mathrm{O}$ in ether, we cannot accurately judge the ether concentrations in the liquid phase that correspond to the above-mentioned P_{ether}. Nevertheless, judging from an estimate by Raoult' s law, we are dealing with small mole fractions of $(\mathrm{C_2H_5})_2\mathrm{O}$ in solution (~ 0.03). The influence of ether on the catalytic activity of $(\mathrm{C_2H_5})_2\mathrm{O}\cdot\mathrm{BF_3}$ is analogous to the influence of water on the acidity of mineral acids (phosphoric, sulfuric, etc.). Such a strong action of ether, even at low concentrations, can be explained only by its basic properties.

Fig. 2. Dependence of the polymerization rate constant of $i\mathrm{C_4H_8}$ in the presence of boron fluoride etherate on the ether pressure in the gas phase.

Figure 3 and Table 1 show the dependence of the polymerization rate constant K_1 on the equilibrium pressure of boron fluoride in the gas phase. At comparatively low $\mathrm{BF_3}$ pressures, a linear dependence is observed between K_1 and $P^{\mathrm{g}}_{\mathrm{BF_3}}$. As $P^{\mathrm{g}}_{\mathrm{BF_3}}$ is raised to 100-200 mm Hg, the linear dependence is disrupted and the value of K_1 increases more slowly than at first. Judging from experiments Nos. 21, 22, and 23, where $P^{\mathrm{g}}_{\mathrm{BF_3}}$ varies from 197 to 290 mm Hg, it may be said that at high pressures of boron fluoride the rate constant does not change (within the accuracy of the experimental error).

At $t = 70^\circ$ and $P_{i\mathrm{C_4H_8}} > 100$-150 mm Hg, deviations are observed

Table 1

Exp. Nos.	$P^0_{BF_3}$	P^0_{ether}	P_{sum}	$P^g_{BF_3}$	P^g_{ether}	$P^g_{e\text{-}t}$	$P^l_{e\text{-}t}$	$P^g_{BF_3} : P^g_{ether}$	$P_{iC_4H_8}$, mm Hg	K_1
1	13.5	80	81	5.25	71.7	4.0	4.25	$7.3 \cdot 10^{-2}$	82	0.24
2	19.0	80	76	5.5	66.5	4.0	9.5	$8.3 \cdot 10^{-2}$	110	0.32
3	21.8	60	67.5	11.5	49.8	6.2	4.0	0.23	108	0.58
4	24.6	80	78	8.4	63.8	5.8	10.4	0.13	157	0.27
5	24.5	81	78.5	8.3	64.7	5.7	10.6	0.13	174.5	0.26
6	25.2	79.7	76.8	8.3	62.6	5.7	11.2	0.13	39	0.21
7	25.0	80	76.5	8.0	63.0	5.5	11.5	0.13	33	0.26
8	24.0	60	64	11.1	47.2	5.7	7.2	0.23	106	1.2
9	33.8	60.5	57.5	12.5	39.2	5.8	15.5	0.32	112	0.99
10	36	60.2	58.8	14.4	38.6	5.8	15.8	0.37	62	1.02
11	47	61	55.0	17.5	31.5	6.1	23.5	0.55	106	1.3
12	47.7	61	53.5	17.25	30.5	5.7	24.7	0.56	64	1.3
13	60	60.5	50.2	22.0	19.5	5.7	32.3	1.1	64	1.6
14	60.5	51.0	50.5	27.1	17.6	5.8	27.5	1.5	62	1.4
15	59.6	20.5	61.5	48	9.0	4.6	7.0	5.3	58	3.6
16	80.4	11	83	74.2	4.8	3.9	2.2	15.5	53	4.5
17	80.6	15.5	84	71.9	6.8	5.3	3.3	10.5	53	3.9
18	82.3	18.0	82.5	71.1	6.3	4.9	6.6	11.3	58	4.5
19	109	20.5	103	92.8	4.3	4.9	10.3	21.6	58	6.4
20	109	20.0	101.5	93.0	4.1	4.3	11.4	22.6	56	
21	–	–	–	253	2.1	5.8	7.1	120	33	7.2
22	–	–	–	290	1.8	5.8	6.4	160	33	11.3
23	–	–	–	215	2.5	5.8	4.7	86	33	12.2

Note. $P^0_{BF_3}$, P^0_{ether}—initial pressures of BF_3 and ether in the reactor; $P^g_{BF_3}$, P^g_{ether}—equilibrium pressures of BF_3 and ether in the reactor; P_{sum}—total pressure in the reactor after admitting BF_3 and ether; $P^g_{e\text{-}t}$—equilibrium pressure of ether in the gas phase; $P^l_{e\text{-}t}$—amount of ether adsorbed on the surface of quartz; K_1—bimolecular constant expressing the decrease in the pressure of $i\mathrm{C}_4\mathrm{H}_8$ in a reactor of volume 1 liter and referred to 1 mole of adsorbed ether.

from bimolecularity of the same character as in the case of phosphoric-acid and sulfuric-acid catalysts ([3],[4]). These deviations are as follows: with increasing $P_{iC_4H_8}$, the bimolecular rate constant K_1 decreases, as does the degree of conversion up to which the kinetic curve can be described by a second-order equation. The experimental data on the dependence of the polymerization rate W on $P_{iC_4H_8}$ are also satisfactorily described by the same empirical equation as for sulfuric-acid and phosphoric-acid catalysts:

Fig. 3. Dependence of the polymerization rate constant of iC_4H_8 in the presence of boron fluoride etherate on the pressure of boron fluoride in the gas phase

Figure 2: Fig. 3. Dependence of the polymerization rate constant of iC_4H_8 in the presence of boron fluoride etherate on the pressure of boron fluoride in the gas phase

Fig. 3. Dependence of the polymerization rate constant of iC_4H_8 in the presence of boron fluoride etherate on the pressure of boron fluoride in the gas phase

$$W = \frac{Aa^2 P_{iC_4H_8}}{(1 + aP_{iC_4H_8})^2},$$

where A and a are parameters.
For example, for a catalyst characterized by pressures in the gas phase: $P^r_{\mathrm{BF3}} =$ 16 mm and $P^r_{\mathrm{ef}} = 15$ mm Hg, when $P_{iC_4H_8}$ is varied from 50 to 390 mm Hg, the bimolecular constant decreases by a factor of 10.

From the data of Table 1 it is seen that boron fluoride etherate is an effective catalyst for the polymerization of iC_4H_8. The etherate, characterized by pressures in the gas phase at 70°: $P^r_{\mathrm{BF3}} = 67$ mm Hg, $P^r_{\mathrm{ef}} = 5.5$ mm Hg, has the same catalytic activity as 70% $\mathrm{H_2SO_4}$, whose acidity function is equal to -6.05.

Judging by its catalytic activity, the etherate should possess the properties of a strong acid. Wichterle (5) showed that in a medium of 100% etherate the indicator benzalacetophenone ($pK_B = -5.6$) is ionized to a considerable extent. To measure the acidity function of the etherate-ether system, we used the following indicators: *o*-nitroaniline; 5-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, and 2,4-dinitroaniline.

In 100% etherate the value

$$\log \frac{C_{\mathrm{BH^+}}}{C_{\mathrm{B}}}$$

for the indicator 2,4-dinitroaniline is equal to 1.8. If, however, as was done by Wichterle, it is assumed that at concentrations close to 100% etherate the pK_B of the indicator is the same as in aqueous solutions, then H_0 of 100% etherate should be equal to -6.2.

Meerwein (6), Greenwood, and Martin (7) believe that the etherate can dissociate with formation of the ion $\mathrm{C_2H_5^+}$. In the case of such ionization, the polymerization products of iC_4H_8 should contain products of conversion of the ions $\mathrm{C_2H_5^+}$ and $\mathrm{C_2H_5OBF_3^-}$ ($\mathrm{C_6H_{12}, C_4H_9OC_2H_5}$). In carrying out a mass-spectral analysis of the polymerization products of iC_4H_8 in the etherate medium, the indicated substances were not found. We assume that ionization of the etherate proceeds at the C—H bond. Isobutylene is ionized in the etherate medium:

$$(C_2H_5)_2OBF_3 + iC_4H_9 \rightleftarrows iC_4H_9^+ + C_4H_9OBF_3^-$$

and further conversion proceeds by the usual acid mechanism.

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