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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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CHEMISTRY

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KINETICS OF THE DEHYDROGENATION OF ETHYLBENZENE TO STYRENE

There is a fairly extensive literature on the catalytic conversion of ethylbenzene to styrene, mainly patent literature, concerning catalysts and the method of dehydrogenation of alkylbenzenes; there are also materials on the study of the equilibrium of the dehydrogenation reaction of ethylbenzene to styrene (1-3). In the present work, the kinetics of the dehydrogenation reaction of ethylbenzene to styrene was investigated for the first time, and the influence of the structure of the alkyl radical on the rate of dehydrogenation was clarified.

The experiments were carried out in a flow system in an apparatus described previously (4), over a mixed oxide catalyst with dilution by water vapor. The procedure for carrying out the experiments was the same as in the dehydrogenation of isopropylbenzene (5). The experiments were conducted with 10 ml of catalyst. The degree of dilution of ethylbenzene with water vapor was kept constant and was 1 : 3 parts by weight. The catalyst obtained from the experiments was colorless. The styrene content in the catalyst was determined by the bromometric method according to Rosenmund (6).

Fig. 1. Logarithmic dependence between $\lg z_2$ and $1/T$

In addition, the catalyst was analyzed by gas-liquid chromatography. Dinonyl sebacate, deposited on diatomaceous brick in an amount of 18%, was used as the liquid phase. To avoid polymerization of the catalyst, Neozone D was added to the liquid phase in an amount of 2%. The contact gas was analyzed on a modified Orsa apparatus for the content of carbon dioxide, olefin hydrocarbons, hydrogen, and saturated hydrocarbons. After each experiment the catalyst was purged with a steam-air mixture and with air. The activity of the catalyst was monitored by carrying out experiments under constant conditions (temperature and space velocity); throughout all the experiments it remained constant.

Figure 2

Figure 2: Figure 2

Fig. 2. Dependence of $\lg k_c$ on $1/T$

The initial ethylbenzene had the following constants: b.p. 135.5°; d_4^{20} 0.8696; n_D^{20} 1.4960; literature data (7): b.p. 136.5°, d_4^{20} 0.869; n_D^{20} 1.4959. The styrene used in the experiments to determine the relative adsorption coefficients had b.p. 144-145°; d_4^{20} 0.9000; n_D^{20} 1.5485; literature data (7): b.p. 145-146°; d_4^{20} 0.9030; n_D^{20} 1.5484.

The kinetics of the dehydrogenation of ethylbenzene was investigated in the temperature range 520-560° and at a space velocity of 800-1000 ml/l • hr. Contact-

gas was evolved at a uniform rate; the evolved gas was measured every 3 min, and the volume was reduced to normal conditions (N.T.P.) and expressed in millimeters per minute. As analysis showed, the evolved gas consisted mainly of hydrogen with a small amount of CO_2 (from 2.3 to 7.4%) and unsaturated hydrocarbons (0.2-0.6%). Saturated hydrocarbons were not detected under these conditions.

The reaction rate was determined from the styrene formed. A close correspondence was observed between the amounts of styrene and hydrogen formed.

From the experimental data, the reaction rate constants were calculated by the equation for monomolecular catalytic reactions in a flow system, derived by one of us ([8]). As we have shown earlier, this equation is valid for the dehydrogenation of hydrocarbons ([9]) and alcohols ([10]) on an oxide catalyst. In the present case this equation has the form:

$$k = 2{,}303\,(z_2 + z_3)\,A_1 \cdot \lg \frac{A_1}{A_1 - m} - m\,(z_2 + z_3 - 1), \qquad (1)$$

where k is the reaction rate constant; z_2 and z_3 are the relative adsorption coefficients of the reaction products—styrene and hydrogen; A_1 is the amount of substance passed per unit time; m is the amount of reaction product formed.

To determine the relative adsorption coefficients of the reaction products—styrene and hydrogen—under analogous conditions, the dehydrogenation rates of the binary mixtures ethylbenzene—styrene and ethylbenzene—hydrogen were measured. The numerical values of the relative adsorption coefficients were calculated from the formula:

$$z = \frac{m_0/m - 1}{100/p - 1}, \qquad (2)$$

where m_0 and m are the amounts of reaction product formed when passing the pure substance and a mixture containing p percent of the reacting substance with the reaction product for which z is being determined.

Table 1

Determination of relative adsorption coefficients in the ethylbenzene–styrene mixture (19.5 mol. % styrene)

T-ra, °C	m_0	(m)	z_2
520	5.4	2.5	4.8
530	8.0	4.3	3.4
540	11.5	7.4	2.3
550	15.0	11.0	1.5

As can be seen from Table 1, the relative adsorption coefficients of styrene vary from 4.8 at 520° to 1.5 at 550°. It was found that the relative adsorption coefficient of hydrogen, equal to 0.7, does not change with temperature. The logarithmic dependence of z_2 on the reciprocal absolute temperature is shown in Fig. 1. The results of experiments on the dehydrogenation of ethylbenzene are summarized in Table 2.

The rate constants calculated from the experimental data according to equation (1) are given in Table 3. In Fig. 2, constructed from the data of Table 3,

Table 2

Dehydrogenation of ethylbenzene. (Feed rate 0.50 ml in 3 min. (1000 ml/l · h), dilution with water vapor 1 : 3 by weight.)

T-ra, °C	Styrene in catalyst, %	H_2 (N.T.P.) in 3 min., ml	Degree of dehydrogenation by H_2, %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %
				CO_2	C H_2	H_2
522	6.0	4.8	5.1	2.3	0.5	97.2
522	6.0					
532	8.0	6.6	7.8	2.6	0.6	96.6
542	12.0	12.0	12.7	4.0	0.6	94.3
544	12.0	12.0	12.7	4.2	0.6	95.1
553	15.5		15.8	5.0	0.4	94.6
563	23.5	23.2	25.1	7.4	0.2	92.4

the dependence of the logarithm of the rate constant on the reciprocal absolute temperature is shown. The points fall on a straight line. The activation energy, calculated from the reaction-rate constants, was found to be 36.1 kcal/mole, and the pre-exponential factor $\lg k_0$ is 7.42. From the values found for the relative adsorption coefficients, the changes in free energy (ΔF), heat content (ΔH), and entropy (ΔS) of adsorption displacement (Table 3) were calculated by the known formulas.

Table 3

Rate constant for the dehydrogenation of ethylbenzene k_c and thermodynamic functions of adsorption displacement of ethylbenzene by styrene

Temp., °C	$k \cdot 10^2$, g/ml • min	ΔF, cal	ΔH, kcal/mole	ΔS, cal/g • mole
520	0.292	2465	32.8	44.5
530	0.370	1950	32.8	43.2
540	0.5120	1344	32.8	42.0
550	0.7800	715.8	32.8	40.7
545	0.6130			

Comparing the results obtained for the dehydrogenation of ethylbenzene to styrene with the data obtained for the dehydrogenation of isopropylbenzene, the kinetics of whose dehydrogenation we studied on the same catalyst sample[5], it can be seen that ethylbenzene is dehydrogenated at a lower rate than isopropylbenzene. Thus, at 520° the rate constant for the dehydrogenation of ethylbenzene is 0.292 ($k_c \cdot 10^2$), while that for isopropylbenzene is 0.7759 ($k_c \cdot 10^2$); at 550° the constants are respectively 0.780 and 1.570. Thus, isopropylbenzene with a branched radical is dehydrogenated at almost twice the rate of ethylbenzene.

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Note: Figure translations are in progress. See original paper for figures.