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Fig. 2. Logarithmic dependence between the reaction-rate constant and $1/T$

Figure 2: Fig. 2. Logarithmic dependence between the reaction-rate constant and $1/T$

Abstract

Full Text

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THE INFLUENCE OF THE STRUCTURE OF ALKYLAROMATIC HYDROCARBONS ON THE KINETICS OF THEIR DEHYDROGENATION

In previous works (^{1},^{2}) we showed that isopropylbenzene, with a branched radical, is dehydrogenated at a higher rate than ethylbenzene, which has a straight chain. It was of interest to investigate the influence of introducing a second radical into the benzene ring on the rate of dehydrogenation of the ethyl radical. For this purpose, the kinetics of the dehydrogenation of ethyltoluene was studied. The experiments were carried out by the flow method in the apparatus described earlier (^{1}), with the same catalyst charge (10 ml). The rate of the reaction was determined from the amount of vinyltoluene formed. A close correspondence was observed between the amounts of vinyltoluene formed and hydrogen evolved. The experimental procedure was the same as previously (^{1}); the degree of dilution with steam was varied from 1 : 16 to 1 : 32 mol and was kept constant in all experiments. The content of vinyltoluene in the catalyzates was determined by the bromometric method according to Galpern (^{3}). In addition, the catalyst was analyzed by gas-liquid chromatography. As the liquid phase we used a mixture of dinonyl didecyl sebacinates deposited on diatomaceous brick in an amount of 18% and containing 2% neozone-D. The contact gas was analyzed as before. By measuring the rates of dehydrogenation of binary mixtures of ethyltoluene–vinyltoluene, the relative adsorption coefficients of the

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reaction product—vinyltoluene—were determined. The initial ethyltoluene had the following constants: b.p. 159-161°, d_4^{20} 0.8660, n_D^{20} 1.4970; literature data: b.p. 161.5°, d_4^{20} 0.8657, n_D^{20} 1.4967.

Vinyltoluene: b.p. 169.5°, d_4^{20} 0.8758, n_D^{20} 1.5406; literature data (4): b.p. 169.0°, d_4^{20} 0.8760, n_D^{20} 1.5403.

Dehydrogenation of ethyltoluene

Experiments with ethyltoluene were carried out in the temperature range 524-560°, at a feed rate of 1000 ml/l • h (0.5 ml in 3 min), with dilution by steam in ratios of 1 : 16 and 1 : 32 mol. The experiments were carried out far from equilibrium, as is evident

Table 1

Dehydrogenation of ethyltoluene*

Temperature, °C	Vinyltoluene in the catalyzate, %	H_2 (NTP) in 3 min, %	Degree of dehydrogenation with respect to H_2, %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %
				CO_2	C H_2	H_2	C H_2 + 2
Dilution with steam 1 : 16 mol.	**Dilution with steam 1 : 16 mol.**	**Dilution with steam 1 : 16 mol.**	**Dilution with steam 1 : 16 mol.**	**Dilution with steam 1 : 16 mol.**	**Dilution with steam 1 : 16 mol.**	**Dilution with steam 1 : 16 mol.**	**Dilution with steam 1 : 16 mol.**
524	13.4	12.8	16.0	8.3	0.2	91.0	0.5
537	19.4	16.6	20.7	8.4	0.2	91.4	0.6
545	22.0	19.3	24.0	8.4	0.2	90.2	0.6
550	27.5	23.3	29.0	8.3	0.4	90.5	0.8
553	30.0	25.7	32.0	8.4	0.4	89.8	0.8
555	30.5	25.5	31.8	8.4	0.3	90.5	0.8
Dilution with steam 1 : 32 mol.	**Dilution with steam 1 : 32 mol.**	**Dilution with steam 1 : 32 mol.**	**Dilution with steam 1 : 32 mol.**	**Dilution with steam 1 : 32 mol.**	**Dilution with steam 1 : 32 mol.**	**Dilution with steam 1 : 32 mol.**	**Dilution with steam 1 : 32 mol.**
525	13.5	11.7	13.4	8.2	0.2	91.0	0.5
549	25.3	22.5	28.0	8.0	0.0	91.0	0.6

Fig. 3. Chromatographic analysis of catalyzates obtained at 580° and at feed rates: a –1000, b –820, and c –570 ml/l • h; the curve peaks correspond respectively: the first to toluene, the second to xylenes, the third to ethyltoluene, the fourth to vinyltoluene.

Figure 3: Fig. 3. Chromatographic analysis of catalyzates obtained at 580° and at feed rates: a –1000, b –820, and c –570 ml/l • h; the curve peaks correspond respectively: the first to toluene, the second to xylenes, the third to ethyltoluene, the fourth to vinyltoluene.

Temperature, °C	Vinyltoluene in the catalyzate, %	H_2 (NTP) in 3 min, %	Degree of dehydrogenation with respect to H_2, %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %	Gas analysis, vol. %
551	27.3	24.7	30.8	8.4	0.2	91.0	0.6
560	32.0	32.0	35.1	8.6	0.2	90.9	0.6

* Feed rate 1000 ml/l • h

When comparing the data obtained with the calculated thermodynamic-equilibrium data for this reaction, given in the paper by Bondarenko et al. (5), it is seen that, under the conditions studied, along with vinyltoluene, small amounts of toluene and xylene are formed as by-products, as was detected by chromatographic analysis. Analysis of the contact gas, which contains small amounts of olefinic (0.2-0.4%) and paraffinic (0.5-0.9%) hydrocarbons, also indicates only slight formation of side decomposition products.

Fig. 3. Chromatographic analysis of catalyzates obtained at 580° and at feed rates: *a* –1000, *b* –820, and *c* –570 ml/l • h; the curve peaks correspond respectively: the first to toluene, the second to xylenes, the third to ethyltoluene, the fourth to vinyltoluene.

The data obtained for the dehydrogenation of ethyltoluene in the temperature range 524-560° are given in Table 1. To determine the relative adsorption coefficients of vinyltoluene, the dehydrogenation rates of ethyltoluene-vinyltoluene mixtures containing 21 mol.% vinyltoluene were measured. Experiments with the mixtures were carried out in the same temperature range (530-560°) as with ethyltoluene, at the same feed rate and with dilution by water vapor. The numerical values of the relative adsorption coefficients, calculated by formula (6), are given in Table 2, from which it is seen that with increasing temperature the relative adsorption coefficients (z_2) of vinyltoluene decrease from 3.8 at 530°

to 1.5 at 560°. When $\lg z_2$ is plotted as a function of the reciprocal absolute temperature, the points fall on a straight line (Fig. 1). The relative adsorption coefficient of hydrogen (z_3) was found to be 0.7; it does not change with temperature.

The data obtained on the kinetics of hydrocarbon dehydrogenation are described by the general kinetic equation for monomolecular reactions in a flow system (7). The rate constants for the dehydrogenation reaction of ethyltoluene are given in Table 2. The logarithmic dependence of the rate constant of the reaction rate on the reciprocal absolute temperature is shown in Fig. 2. The points fall on a straight line; the Arrhenius equation is obeyed. The activation energy, calculated from the reaction rate constants, is 34.6 kcal/mol, and $\lg k_0 = 7.3$.

Table 2

Kinetic and thermodynamic functions of the adsorption displacement of ethyltoluene by vinyltoluene

T, °C	z_2	$k_c \cdot 10^2$, g/ml in 3 min	$-\Delta F$, kcal/mol	ΔH, kcal/mol	ΔS, cal/deg · mol
530	3.8	0.731	1914	32.3	42.6
540	2.6	0.969	1566	32.3	41.8
550	2.0	1.274	1132	32.3	40.6
560	1.5	1.704	668.3	32.3	39.6

Using the values found for the relative adsorption coefficients of vinyltoluene on the active surface of the catalyst, we found the changes in free energy, heat content, and entropy upon adsorption displacement from the catalytic surface (Table 2). Table 3 gives, for comparison, the rate constants for the dehydrogenation of ethylbenzene and ethyltoluene, from which it is seen that the rate of dehydrogenation of ethyltoluene is greater than that of ethylbenzene. Thus, the results obtained indicate that, upon introduction of a methyl radical into the benzene ring, the rate of dehydrogenation of the ethyl radical increases.

Table 3

Rate constants for the dehydrogenation of ethylbenzene and ethyltoluene

T, °C	ethylbenzene, $k_c \cdot 10^2$, g/ml in 3 min	ethyltoluene, $k_c \cdot 10^2$, g/ml in 3 min
530	0.376	0.731
540	0.5120	0.969
550	0.7800	1.274

T, °C	ethylbenzene, $k_c \cdot 10^2$, g/ml in 3 min	ethyltoluene, $k_c \cdot 10^2$, g/ml in 3 min
560	1.055	1.704

It is known from the literature (8) that vinyltoluene may be of considerable interest in the synthetic rubber industry for obtaining copolymers, and also in perfumery and other fields (9). Therefore it was of interest to study the dehydrogenation of ethyltoluene on a mixed oxide catalyst at elevated temperature. For this purpose, experiments were carried out at 580° and at different feed rates of ethyltoluene (1000, 820, and 570 ml/l • h). The results of the balance experiments are given in Table 4, from which it is seen that at the same temperature (580°), with decreasing

Table 4

Catalytic dehydrogenation of ethyltoluene at 580° and with dilution by steam 1 : 4 (weight ratio)

Feed rate, ml/l• h	Catalyst yield, wt. %	vinyltoluene, wt. %	C_6H_6, wt. %	toluene, wt. %	xylene, wt. %	Yield of vinyltoluene based on passed and decomposed ethyltoluene, wt. %	CO_2, vol. %	C_nH_{2n}, vol. %	H_2, vol. %	C_nH_{2n+2}, vol. %
1000	98.0	42.3	–	0.4	4.4	42.8	86.1	11.3	0.6	85.0
820	97.8	53.7	–	1.0	8.0	51.3	81.2	11.7	1.0	84.5
570	97.5	58.0	0.1	1.4	10.8	56.0	80.7	13.3	0.8	81.8

With a decrease in the flow rate from 1000 to 570 ml/l • h, the yields of vinyltoluene based on ethyltoluene passed increase from 42.8 to 56.8%. At the same time, the yields based on decomposed ethyltoluene decrease from 86.1 to 80.7%, which indicates the formation of side reaction products. The results of analysis of the catalyzates on a chromatograph (Fig. 3) show that, as the flow rate decreases, the amount of toluene increases from 0.6 to 1.4% (at a rate of 570 ml/l • h) and that of xylene from 4.3 to 10.8%. At a flow rate of 570 ml/l • h, in addition, 0.1% benzene is formed. The data presented show that, on an oxide catalyst, vinyltoluene can be obtained in high yields at 580° and at higher flow rates of ethyltoluene.

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