



ISOMERIZATION OF CHLORO-OLEFINS OF ALLYL STRUCTURE BY HETEROGENEOUS CATALYSIS

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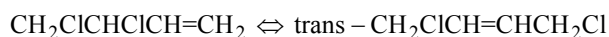
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The reaction kinetics of the isomerization of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2 was investigated using gas-liquid chromatography in the temperature range of 70-100 °C. Fe₂O₃/SiO₂ was used as a catalyst. Fe₂O₃/SiO₂ solid acid catalyst has been prepared by the support saturation method, tested in the isomerization of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2. This catalyst shows a high activity opposite to pure SiO₂ in this reaction. The present investigation focuses on the reactivity of silica supported ferric oxide with iron content 5 wt. % in the isomerization of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2. The activation parameters have been evaluated under optimized conditions, using the Arrhenius and Eyring plots.

INTRODUCTION

The isomerization of halogen-containing alkenes plays an important role in chemical synthesis. One of the processes is the isomerization of 3,4-dichlorobutene-1 (3,4-DCB-1) into 1,4-dichlorobutene-2 (1,4-DCB-2), which is a useful and efficient step in the synthesis of styrene-butadiene rubber:



This reaction was earlier studied using acid homogeneous catalysts¹ and homogeneous complexes of transition metals;^{2, 3} recently heterogeneous catalysts and nanocomposites have also been employed for this reaction.^{4,5} Heterogeneous catalysts in an insoluble form have many advantages over liquid acid systems, because they cause a lower corrosion rate, ensure safer handling of the catalyst and simple catalyst regeneration, and are easily recyclable. Iron (III) oxide (Fe₂O₃) is used as a catalyst in many chemical reactions, such as dehydration of ethyl benzene, CO hydrogenation, alkylation, and the

processes where halogen-containing alkenes were used as substrates,^{6, 7} therefore, this compound seems to be an appropriate catalyst for the conversion of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2, because this reaction includes the breaking of the C-Cl bond. The process is structurally sensitive and can be promoted with ultradisperse metals or metal oxides, among which iron oxides are the most efficient. In this article the aim is to investigate the isomerization of 3,4-DCB-1 into 1,4-DCB-2 by heterogeneous acid catalysis Fe₂O₃/SiO₂. Thermodynamic and kinetic parameters are also reported.

EXPERIMENTAL

Commercial KSKG Silica gel was used as a support. Its specific surface area, *S*, determined by the thermal desorption of nitrogen, was found to be 364 m²/g. The color of the investigated catalyst was yellow- brown. The nature of the surface of catalyst strongly dependence on ratio $\frac{\text{Fe}}{\text{SiO}_2}$.

With decreasing of total iron content (≤ 5 wt. %) the relative content of smaller clusters of γ - ferric oxide increased. γ -ferric oxide particles supported on silica are the most active

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catalysts for isomerization of 3,4-DCB-1 into 1,4-DCB-2.⁸ In this work the catalyst with Fe content 5 wt % was prepared. To determine the structure of iron-containing particles on the catalyst surface, we examined the catalyst containing 5 wt % of Fe by Mössbauer spectroscopy.⁹⁻¹¹ In the preparation of the catalyst by the support saturation method, the solid support was heated in an iron (III) chloride solution at 100°C for at least 6 hours. The progress of isomerization of 3,4-DCB-1 into 1,4-DCB-2 was investigated in the temperature interval of 70 to 100°C with 0.03, 0.04 and 0.05 g catalyst in 0.3-mL portion (0.0028 mol) of freshly distilled 3,4-dichlorobutene-1. The following procedure was used to obtain catalytic data. An accurately weighed portion for example 0.03 g (2.7×10^{-5} mole Fe) of the catalyst sample was placed in a glass ampoule and 0.3-mL of freshly distilled 3,4-dichlorobutene-1 was added into the ampoule. Then, the ampoule was sealed, and the

reaction mixture was stirred under thermostatic conditions at temperatures varied from 70 to 100°C. After a certain time, the sample was taken off from the thermostat and cooled. The composition of products was determined by gas-liquid chromatography on a Tsvet-100 chromatograph with a flame ionization detector, equipped with a glass column (180 × 0.25 cm) packed with a 5% SE-30 stationary phase applied on Chromaton N-AW-DMCS. The column was stabilized at 70°C under a helium flow. Five to eight ampoules were used to obtain one catalytic curve. The major product of the reaction was *trans*-1,4-dichlorobutene-2; the amount of *cis*-1,4-dichlorobutene-2 produced in the reaction was less than 2%. Other products in the isomerization reaction were not detected. A typical chromatogram for 5 wt % Fe on the surface of SiO₂ at 90 °C after a 110 minute is presented in Fig 1.

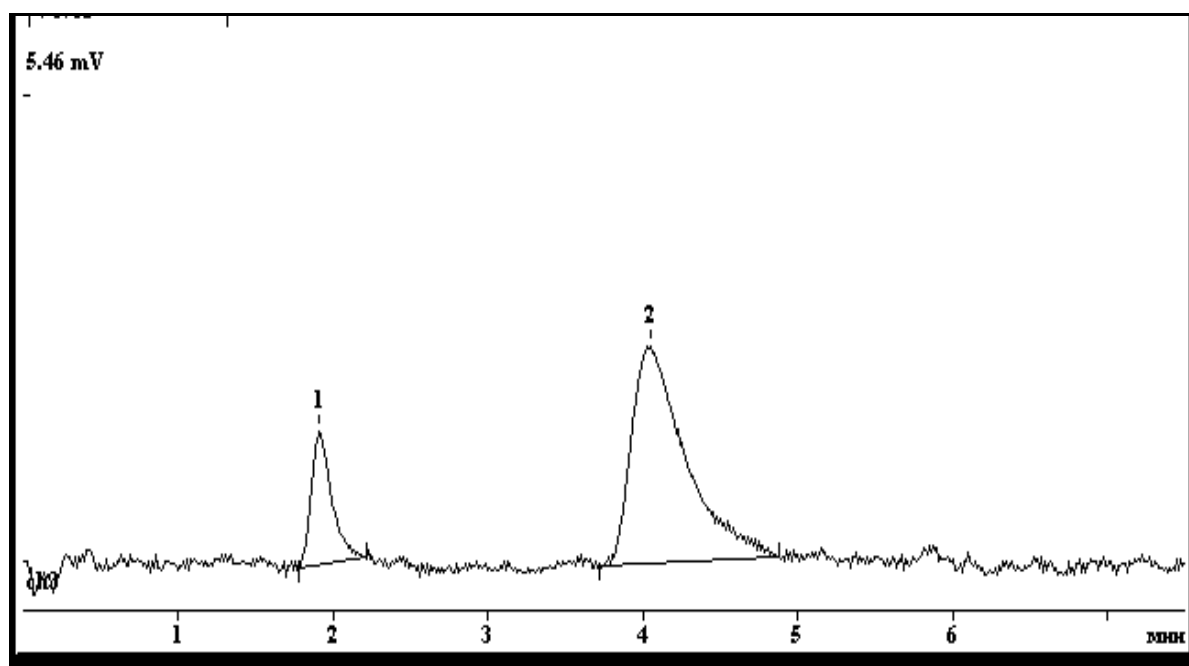


Fig. 1 – The chromatogram of isomerization reaction of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2 at 90 °C after 110 minute.

The selectivity of the main product formed; mention any other product formed is because of the information of stable allyl carbocation (thermodynamic stability). In the *trans* product opposite with *cis* product, bulky groups have most distance and least repellent. Therefore the main product is *trans*.

RESULTS AND DISCUSSION

The progress of isomerization of 3,4-DCB-1 into 1,4-DCB-2 was followed by yield of 1,4-dichlorobutene-2 of the various amounts of the catalysts at different temperatures with time (min) according to percent or conversion of the reactant and as typical the results at 80°C are presented

graphically in Fig. 2. These quantities were defined from a parity of the areas of peaks with considering of concentration initial reactant.

The catalytic activity of the obtained catalysts can be determined by the kinetic curves of isomerization in the region of maximum reaction rate using the following equation

$$A = \frac{C_{1,4-DCB}}{n_{Fe} \times t}$$

where $C_{1,4-DCB}$ is the mole fraction of the product, n_{Fe} is the amount of iron applied on the support surface (mol), and t is time (h). The experimental results are presented in Table 1. (Data were reported with accuracy of $\pm 10\%$).

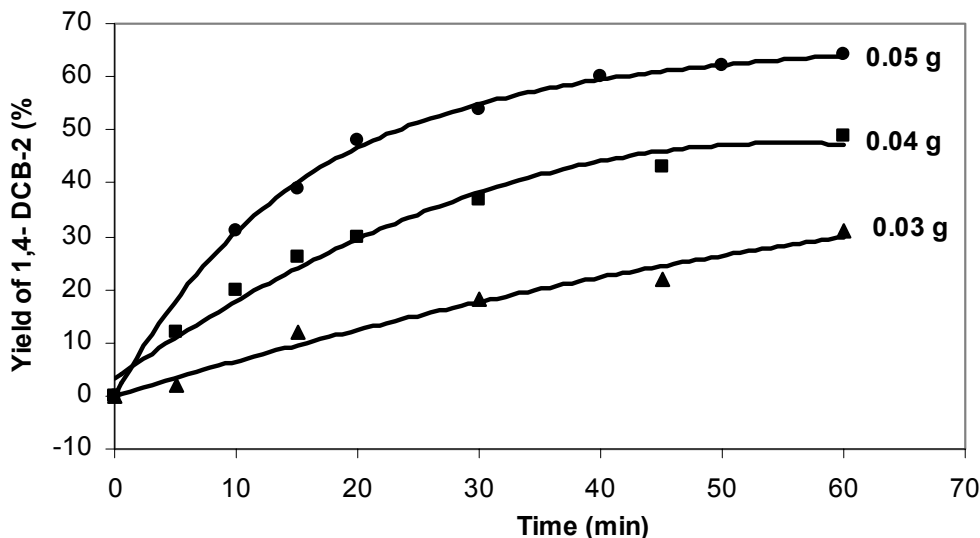


Fig. 2 – Yield of 1,4-dichlorobutene-2 vs. t (min) obtained at 80°C.

Table 1

Catalytic activity of the $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalysts [$\text{mol product} (\text{mol Fe})^{-1} \text{h}^{-1}$] containing various amounts of catalysts at different temperatures

T (°C)	$\text{Fe}_2\text{O}_3/\text{SiO}_2$ (g)		
	0.05	0.04	0.03
100	228 ± 23	212 ± 21	146 ± 15
90	160 ± 16	136 ± 14	91 ± 10
80	93 ± 9	76 ± 8	41 ± 4
70	59 ± 6	44 ± 5	12 ± 1

According to the results, the catalytic activity of the studied samples is decreased with decreasing amount of catalysts and temperature.

The reaction exhibit a reversible first order kinetics with the following rate law:

$$\ln \left[\frac{C_\infty - C_t}{C_\infty - C_0} \right] = -(k_1 + k_{-1}) \cdot t = -k_{\text{eff}} \cdot t$$

where C_t , C_0 and C_∞ are the product concentration at time t , initial time ($t = 0$), and the equilibrium state of the reaction; k_1 , k_{-1} , and k_{eff} are the direct, indirect, and effective rate constants of the reaction, respectively. The values of C_t can be found experimentally, and the thermodynamic equilibrium constants at different temperatures are known^{12,13}, therefore, rate constants k_1 , k_{-1} , and k_{eff} can be determined. Obviously, the plots of

$\ln \left[\frac{C_\infty - C_t}{C_\infty - C_0} \right]$ vs. t (s) should be linear. As a typical

for 0.04 g catalyst at 80°C, results are presented in Fig 3. Similarly, the direct, indirect and effective

rate constants at different temperatures in the region of maximum reaction rate are obtained. The values being reported in Table 2.

One can write the following Arrhenius equation

$$\ln k = \ln A - \frac{E_a}{RT}$$

and as such a plot of $\ln k$ vs. $1/T$ will give a straight line. From the slope and intercept of this plot, the direct (E_{a1}), indirect ($E_{a,-1}$), effective activation energy ($E_{a,\text{eff}}$) and frequency factor (A) may be calculated, respectively. Results are given in Table 3 and also for 0.03g catalyst displayed graphically in Fig. 4.

The Eyring equation¹⁴ may be suitably applied in the flowing form:

$$k = \frac{RT}{Nh} \exp (T\Delta S^* - \Delta H^*)/RT$$

where k is the rate constant and the other symbols have their usual significance.

Table 2

Rate constants of isomerization reaction 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 with the various amounts of catalysts at different temperatures

$t, ^\circ\text{C}$	$k_{ef} \times 10^5 \text{ (s}^{-1}\text{)}$	$k_1 \times 10^5 \text{ (s}^{-1}\text{)}$	$k_{-1} \times 10^5 \text{ (s}^{-1}\text{)}$
		0.05 g	
100	280 ± 28	215 ± 21	65 ± 6
90	150 ± 15	119 ± 12	31 ± 3
80	100 ± 10	81 ± 8	19 ± 2
70	70 ± 7	58 ± 9	12 ± 1
		0.04 g	
100	220 ± 22	169 ± 17	51 ± 5
90	110 ± 11	87 ± 9	23 ± 2
80	70 ± 7	57 ± 6	13 ± 1
70	40 ± 4	33 ± 3	7 ± 0.7
		0.03 g	
100	170 ± 17	131 ± 13	39 ± 4
90	70 ± 7	56 ± 5	14 ± 1.4
80	40 ± 4	32 ± 3	8 ± 0.8
70	20 ± 2	16 ± 2	4 ± 0.4

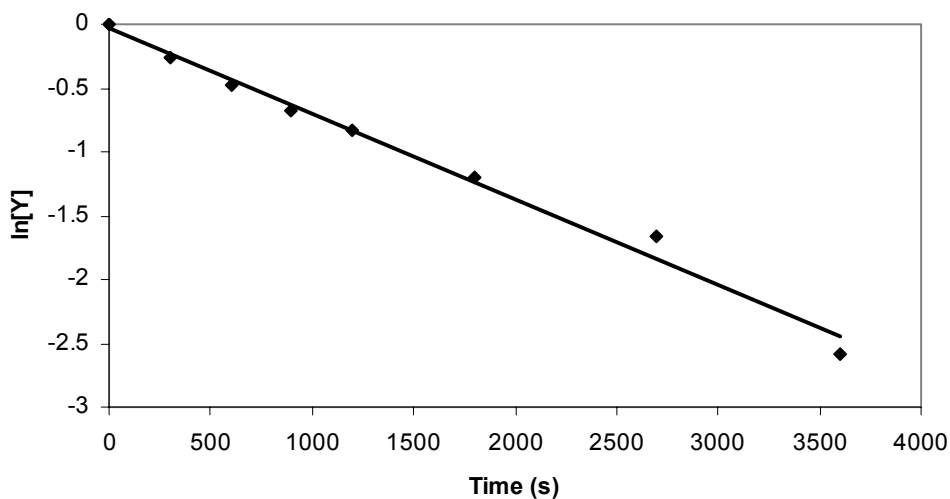


Fig. 3 – Dependence of $\ln \left[\frac{C_\infty - C_t}{C_\infty - C_0} \right] = \ln[Y]$ vs. $t(s)$ for 0.04 g catalyst at 80°C .

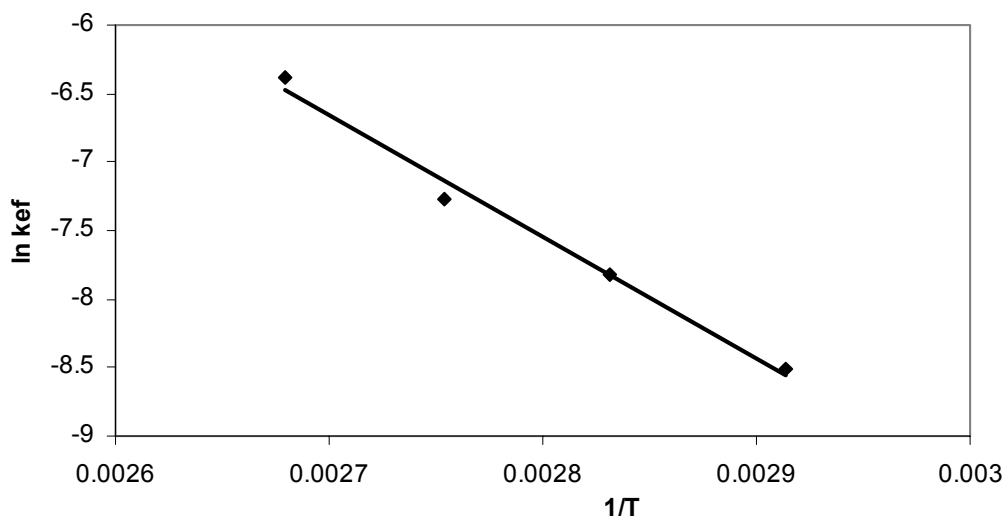


Fig. 4 – Arrhenius plot $\ln k_{ef}$ vs. $1/T$.

The equation leads to:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(-\frac{\Delta H^*}{RT}\right) + \left(\frac{\Delta S^*}{R}\right)$$

Thus a plot of $\ln(k/T)$ vs. $1/T$ should give a straight line, the slope and intercept of which may be used to compute direct (ΔH_1^*), indirect

(ΔH_{-1}^*), effective enthalpy of activation (ΔH_{ef}^*) and direct (ΔS_1^*), indirect (ΔS_{-1}^*) and effective entropy of activation (ΔS_{ef}^*) values, respectively. As a typical for 0.03 g catalyst dependence of $\ln(k_{ef}/T)$ vs. $1/T$ displayed graphically in Fig 5. The calculated values are presented in Table 3.

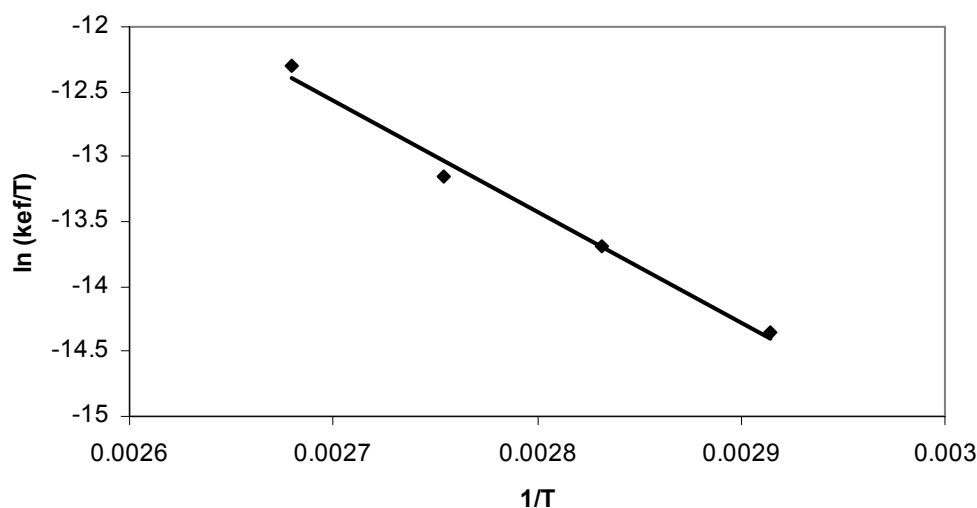


Fig. 5 – Plot of Eyring $\ln(k_{ef}/T)$ vs. $1/T$.

Table 3

Activation parameters for isomerization of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 by $\text{Fe}_2\text{O}_3/\text{SiO}_2$

	$\text{Fe}_2\text{O}_3/\text{SiO}_2$ (g)		
	0.05	0.04	0.03
Ea_{ef}	48 ± 5	59 ± 6	74 ± 7
Ea_1	46 ± 5	57 ± 6	72 ± 7
Ea_{-1}	59 ± 6	69 ± 7	84 ± 8
ΔH_{ef}^*	45 ± 4	56 ± 6	71 ± 7
ΔH_1^*	43 ± 4	54 ± 5	69 ± 7
ΔH_{-1}^*	56 ± 6	66 ± 7	81 ± 8
ΔS_{ef}^*	-0.175	-0.148	-0.109
ΔS_1^*	-0.184	-0.157	-0.119
ΔS_{-1}^*	-0.159	-0.133	-0.095
$A_{ef} \times 10^{-5}$	0.153	3.92	372

The Mössbauer spectrum of the catalyst has a doublet structure (Fig. 6), which is satisfactorily approximated with a doublet model with relative areas of 51 and 49%; the spectral parameters are

presented in Table 4. The obtained data correspond to the octahedral structure of $\gamma\text{-Fe}_2\text{O}_3$ in a superparamagnetic state, which formed in the synthesis of the catalysts. The doublet with the

smaller value of quadrupole splitting corresponds to the iron atoms inside the Fe_2O_3 particle, while

the doublet with the higher value represents the iron atoms situated on the particle surface¹⁵.

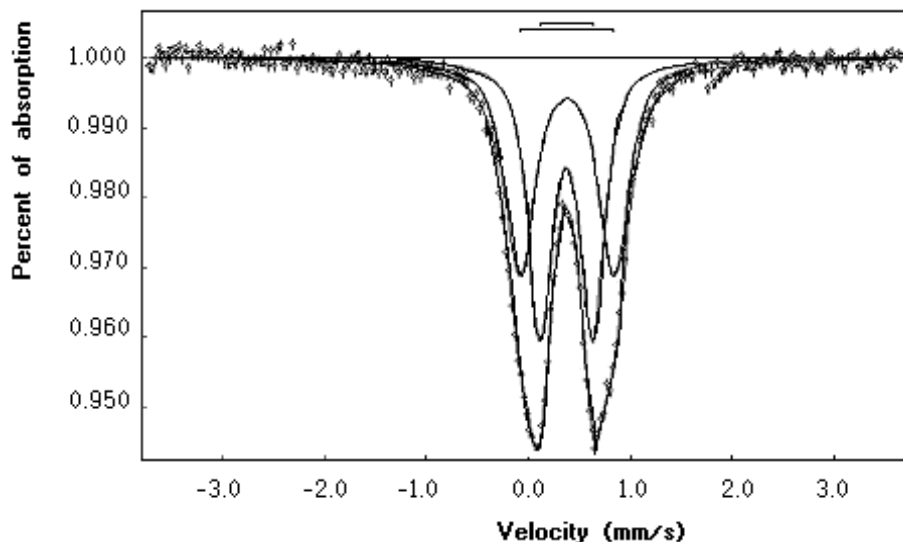


Fig. 6 – Mössbauer spectroscopy for $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalyst.

Table 4

Parameters of the Mössbauer spectrum for $\text{Fe}_2\text{O}_3/\text{SiO}_2$ catalyst

Catalyst	Isomer shift δ (mm/s)	Electric quadrupole splitting Δ (mm/s)	Linewidth Γ_{exp}	Doublet areas (%)
$\text{Fe}_2\text{O}_3/\text{SiO}_2$	0.38 ± 0.01	0.52 ± 0.01	0.29 ± 0.01	51
	0.38 ± 0.01	0.92 ± 0.01	0.35 ± 0.01	49

The procedures used for preparing Fe_2O_3 -containing catalysts in the cited and other works consisted of several stages including high-temperature calcination of the treated support¹². The development of a procedure performed under milder conditions would greatly contribute to further study of such an efficient catalyst. The advantages of this catalyst is simplicity of production and high reactivity for the isomerization of 3,4-dichlorobutene-1 into 1,4-dichlorobutene-2.

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