



Kinetics of Inversion of Dichlorobutene in the Heterogeneous System

N. SAMADANI LANGEROODI

Chemistry Department, Science Faculty, Golestan University, Gorgan, Iran

Corresponding author: Tel./Fax: +98 171 4427040; E-mail: nsamadani@yahoo.com

(Received: 5 July 2011;

Accepted: 17 January 2012)

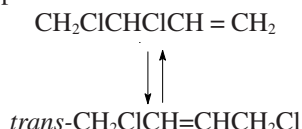
AJC-10993

The reaction kinetics of the isomerization of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 was investigated by using gas-liquid chromatography in presence of $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ as solid catalyst. At the optimizing conditions, the catalytic activity, rate constants of reaction and activation energy have been evaluated using kinetic equations. The structure of the catalyst was investigated by using Mossbauer spectroscopy.

Key Words: Isomerization of chloroolefins, Kinetics, Mossbauer spectroscopy.

INTRODUCTION

The isomerization of allyles halogen-containing derivatives have an important role in the chemical synthesis. One of the isomerization reaction is 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2, which provides a useful and efficient step in the synthetic process of caoutchouc:



This reaction was investigated by acidic homogeneous catalysts and homogeneous complexes of transition series¹⁻⁵. Recently heterogeneous catalysts, nonmetals and nanocomposites⁶⁻⁸ have also been employed for this reaction. 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, simple catalyst regeneration and are easily recyclable. Since in most of the chemical reactions such as dehydration, alkylation and in the process with olefins halogen-containing derivatives as a substrate, iron oxide (Fe_2O_3) was used as a catalyst^{9,10}. It seems this compound can be used an appropriated catalyst for conversion of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2. In this work, an attempt has been made to investigate the conversion of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 by heterogenous acid catalysis $\text{Fe}_2\text{O}_3/\text{ZrO}_2$.

EXPERIMENTAL

Commercial zirconia (zirconium oxide TY 6-09-2486-77) was used as a support. Its specific surface area, s , determined by the thermal desorption of nitrogen equaled 15.32

m^2/g . In the preparation of the catalysts by support saturation method the solid supported solution of $\text{FeCl}_3(\text{III})$ was heated at 100 °C for 6 h. The properties of this catalyst (5 Fe on the surface of ZrO_2 , % mass) was investigated for the isomerization reaction of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 in the range of 25-55 °C. The major product of reaction is *trans*-1,4-dichlorobutene-2 and *cis*-1,4-dichlorobutene-2 produced less than 2 %. Other products in the isomerization reaction was not observed. The analysis of product was carried out by gas-liquid chromatography.

RESULTS AND DISCUSSION

The effect of temperature on the rate of isomerization reaction of 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2 was shown in Fig. 1. In this figure the Y axis shows amount of product in various temperatures and times according to per cent or conversion of the reactant. It is clear that the rate of isomerization reaction is increases with increasing temperature.

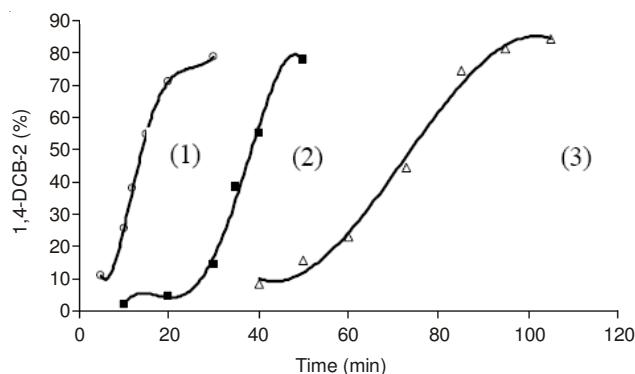


Fig. 1. Curve of product percentage of 1,4-dichlorobutene-2 vs. t(min) in the (1) 55 °C (2) 40 °C and (3) 25 °C

Catalytic activity of catalyst: The catalytic activity of catalyst can be determined by kinetic curves of isomerization reaction in the maximum area of rate reaction using the following equation:

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

where, $C_{1,4\text{-dichlorobutene-2}}$ and n_{Fe} , are defined the mole fraction of product and iron on the surface of support in t time (h). The experimental results illustrated in Table-1. According to results, the catalytic activity is decreased with decreasing temperature.

t (°C)	A
55	272 ± 27
40	140 ± 14
25	81 ± 8

Kinetics of isomerization 3,4-dichlorobutene-1 to 1,4-dichlorobutene-2: The reaction exhibits the reversible first order behavior 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 concentration product at time 't' (min), initial time ($t=0$) and equilibrium state reaction. k_1 , k_{-1} and k_{eff} are the direct, indirect and effective rate constants of reaction. By knowing that c_t (experimental) and thermodynamically equilibrium constants at different temperatures^{11,12} were determined k_1 , k_{-1} and k_{eff} .

It is clear that the plots of $\ln \left[\frac{c_\infty - c_t}{c_\infty - c_0} \right]$ vs. t (s) should be linear. For example in Fig. 2. is presented the plot of

$\ln \left[\frac{C_\infty - C_t}{C_\infty - C_0} \right] = \ln [Y]$ vs. t (s) at 55 °C. Similarly, the direct,

indirect and effective rate constants at different temperatures are obtained. The values being reported in Table-2. By applying the Arrhenius equation to the experimental data, *i.e.*

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

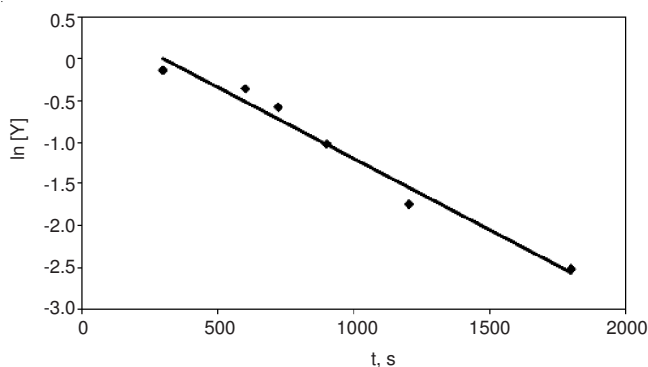


Fig. 2. Dependence of $\ln \left[\frac{C_\infty - C_t}{C_\infty - C_0} \right] = \ln [Y]$ vs. t (s) at 55 °C

TABLE-2
DIRECT, INDIRECT AND EFFECTIVE RATE CONSTANTS OF ISOMERIZATION REACTION 3,4-DICHLOROBUTENE-1 to 1,4-DICHLOROBUTENE-2 AT VARIOUS TEMPERATURE

t (°C)	(s-1) × 10 ⁵ k _{ef}	(s ⁻¹) × 10 ⁵ k ₁	(s ⁻¹) × 10 ⁵ k ₋₁
5 % Fe/ZrO ₂			
55	170 ± 17	146 ± 15	24 ± 2
40	110 ± 11	99 ± 10	11 ± 1
25	60 ± 6	56 ± 6	4 ± 0.4

The direct (E_{a1}), indirect ($E_{a,-1}$) and effective activation energy ($E_{a,\text{eff}}$) were obtained (Table-3). We also examined the structure of active phase from by Mossbauer spectroscopy^{13,14}. Mossbauer spectroscopy for 5 Fe on the surface of ZrO₂, % mass catalyst is presented in the Fig. 3. In Table-4. The parameters of Mossbauer spectroscopy are reported. These parameters are represented the octahedral structure of $\gamma\text{-Fe}_2\text{O}_3$ with superconducting magnets, which formed in the process synthesis of catalysts.

TABLE-3
DIRECT, INDIRECT AND EFFECTIVE ACTIVATION ENERGY OF ISOMERIZATION REACTION 3,4-DICHLOROBUTENE-1 to 1,4-DICHLOROBUTENE-2

E _{ef} (kJ/mol)	E _{a1} (kJ/mol)	E _{a,-1} (kJ/mol)
28 ± 3	26 ± 3	48 ± 5

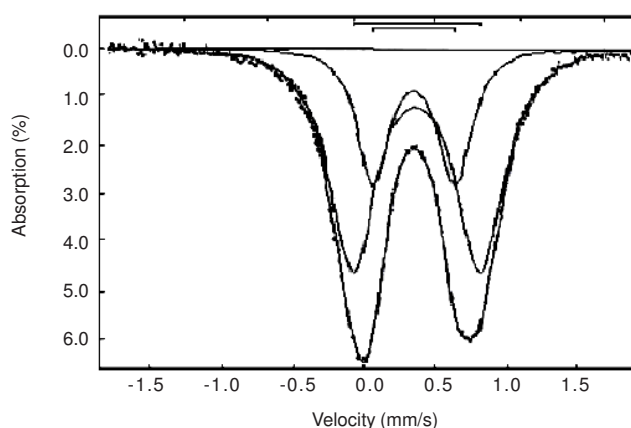


Fig. 3. Mossbauer spectroscopy for 5 Fe on the surface of ZrO₂, % mass

TABLE-4
PARAMETERS OF MOSSBAUER SPECTROSCOPY

δ , mm/s (Chemical shift)	Δ , mm/s (Quadrupole effects)	Area (%)
0.38 ± 0.1	0.90 ± 0.1	69
0.36 ± 0.1	0.58 ± 0.01	31

Conclusion

These results were indicated the present catalyst in this research work have many advantage such as, high catalytic activity (even in the room temperature), simple preparation method and the per cent of major product at optimize temperature and time.

REFERENCES

1. A.Yu. Bogomolov, P.V. Gerasimov, W. Smirnov and T.N. Rostovshchikova, *Kinet. Catal.*, **36**, 607 (1995).
2. A.Yu. Bogomolov, V.V. Smirnov, T.N. Rostovshchikova and P.V. Gerasimov, *Kinet. Catal.*, **36**, 232 (1995).

3. V.V. Smirnov, E.N. Golubeva and T.N. Rostovshchikova, *Kinet. Catal.*, **33**, 58 (1992).
4. T.N. Rostovshchikova, V.V. Smirnov and E.V. Vovk, *Kinet. Catal.*, **33**, 682 (1992).
5. T.N. Rostovshchikova, V.V. Smirnov and A. Yu. Bogomolov, *Vestn. Mosk. Univ., Ser. 2. Khim.*, **2**, **36**, 145 (1995).
6. T.N. Rostovshchikova, V.V. Smirnov and A.I. Kokorin, *J. Mol. Catal. A: Chem.*, **129**, 141 (1998).
7. T.N. Rostovshchikova, V.V. Smirnov, V.M. Kozhevnikov, D.A. Yavsin and S.A. Gurevich, *Kinet. Catal.*, **44**, 555 (2003).
8. L.I. Trakhtenberg, G.N. Gerasimov, V.K. Potapov, T.N. Rostovshchikova, V.V. Smirnov and V. Yu. Zufman, *Vestn. Mosk. Univ., Ser. 2. Khim.*, **42**, 325 (2001). (in Russian).
9. C. Kurts, Y. Arita, W. Weiss, W. Ranke and R. Schlogel, *Topics Catal.*, **14**, 111 (2001).
10. H. Hayashi, L.Z. Chen, T. Tago, M. Kishida and K. Wakabayashi, *Appl. Catal. A: Gen.*, **231**, 81 (2002).
11. T.N. Rostovshchikova, V.V. Smirnov, M.V. Tsodikov, O.V. Bukhtenko, Y.V. Maksimov, O.I. Kiseleva and D.A. Pankratov, *Russ. Chem. Bull. Int. Ed.*, **54**, 1418 (2005).
12. E.M. Asatryan, N.L. Saakyan, E.V. Golneva and G.T. Martirosyan, *Arm. Khim. Zhur.*, **39**, 584 (1986).
13. N.N. Greenwood, *The Mossbauer Spectra of Chemical Compounds*, Chemistry in Britain, Vol. 3, p. 56 (1967).
14. I.P. Suzdalev, *Dynamic Effects in the γ -Resonance Spectroscopy Atomized*, p. 197 (1979).