Isomerization of 3,4-Dichloro-1-butene into 1,4-Dichloro-2-butene by Heterogeneous Catalysis

NARGES SAMADANI LANGEROODI

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

Summary: The isomerization of 3,4-dichloro-1-butene into 1,4-dichloro-2-butene was investigated by gas-liquid chromatography in the temperature range of 60-90 °C. Fe_2O_3/TiO_2 was used as a catalyst. Fe_2O_3/TiO_2 solid acid catalyst has been prepared by the support saturation method, tested in the isomerization of 3,4-dichloro-1-butene into 1,4-dichloro-2-butene. This catalyst shows a high activity opposite to pure titania in this reaction. The present investigation focuses on the reactivity of titatia supported ferric oxide with iron contents of 5 wt. % in the isomerization of 3,4-dichloro-1-butene into 1,4-dichloro-2-butene. 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-dichloro-1-butene (3,4-DCB-1) into 1,4-dichloro-2-butene (1,4-DCB-2), which is a useful and efficient step in the synthesis of styrene-butadiene rubber:

$$CH_2ClCHClCH = CH_2$$

$$\updownarrow$$

$$trans - CH_2ClCH = CHCH_2Cl$$
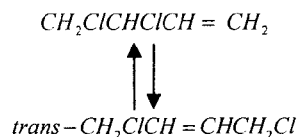
This reaction was earlier studied using acid homogeneous catalysts [1] and homogeneous complexes of transition metals [2, 3]. Recently, heterogeneous catalysts and nanocomposites have also been employed for this reaction [4, 5]. Heterogeneous catalysts in an insoluble form have many advantages over liquid 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 (Fe_2O_3) is used as a catalyst in many chemical reactions, such as dehydration of ethylbenzene, 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-dichloro-1-butene to 1,4-dichloro-2-butene, 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. 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 support. The development of a procedure performed under milder conditions would greatly contribute to further study of such an efficient catalyst. In this article the aim was to prepare a Fe_2O_3/TiO_2 heterogeneous catalyst using simple procedure and to investigate its properties in the catalytic isomerization of 3,4-dichloro-1-butene into 1,4-dichloro-2-butene.

Results and Discussion

The effect of the catalyst, bearing different temperature on the studied reaction rate are shown in (Fig. 1). In this figure the Y axis shows amount of product in various temperatures and times according to percent or conversion of the reactant. The percent of initial reactant that converted to product is called conversion of the reactant. These quantities were defined from a parity of the areas of peaks with considering of concentration initial reactant.

It is rather predictable that the rate of isomerization reaction increased with the increase of temperature.

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
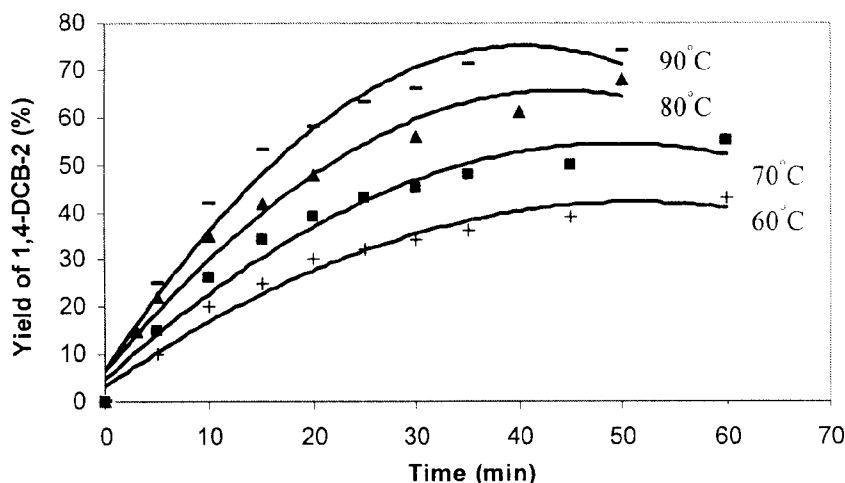
Fig.1:   Yield of 1,4-dichloro-2-butene vs. t(min) obtained using the 5 wt % Fe_2O_3/TiO_2 catalyst in the temperature range of 60-90°C.

opposite to cis product, bulky groups have more distance and less repellant. Therefore the main product is trans.

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

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

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 [8, 9]; 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. For example, the plot of $\ln\left[\frac{C_\infty - C_t}{C_\infty - C_0}\right] = \ln[Y]$ vs. t (s) is presented at 80°C (Fig. 2). 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-1.
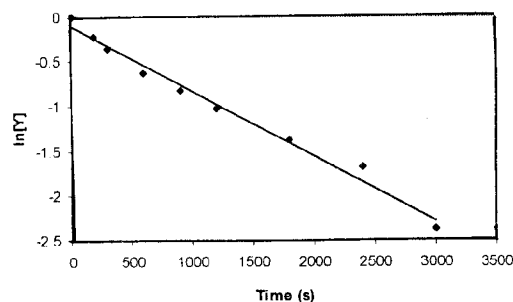

Fig. 2:   Dependence of $\ln\left[\frac{C_\infty - C_t}{C_\infty - C_0}\right] = \ln[Y]$ vs. t (s)

for the 5 wt % Fe_2O_3/TiO_2 catalyst at 80°C.

Table-1: The direct, indirect and effective rate constants of isomerization reaction 3, 4- DCB-1 to 1, 4- DCB-2 at various temperatures.

t (°C)	$k_{ef} \times 10^5$ (s^{-1})	$k_1 \times 10^5$ (s^{-1})	$k_{-1} \times 10^5$ (s^{-1})
90	110±11	85±8.5	22±2
80	80±8	61±6	14±1.4
70	60±6	46±4.6	11±1
60	40±4	31±3	7±0.7

Using the obtained data on the rate constants and applying the Arrhenius equation, that is, $\ln k = \ln A - \frac{E_a}{RT}$ the direct (Ea_1), indirect (Ea_{-1}) and effective activation energy (Ea_{eff}) can be determined. The calculated values are presented in Table-2.

Table-2: Direct, indirect, and effective activation energy of isomerization of 3,4-dichloro-1-butene to 1,4-dichloro-2-butene in the temperature range of 60-90 °C.

E_{eff} (kJ/mol)	Ea_1 (kJ/mol)	Ea_{-1} (kJ/mol)
33.45±4	33.36±4	37.12 ± 4

The Eyring equation [10] may be suitably applied in the following form:

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

The equation leads to:

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

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 enthalpy of activation, ΔH^* and entropy of activation. ΔS^* values, respectively. For example dependence of $\ln(k_{ef}/T)$ vs. 1/T displayed graphically in (Fig. 3). The direct (ΔH_1^*, ΔS_1^*), indirect (ΔH_{-1}^*, ΔS_{-1}^*) and effective enthalpy and entropy of activation (ΔH_{ef}^*, ΔS_{ef}^*) can be determined. The calculated values are presented in Table-3.
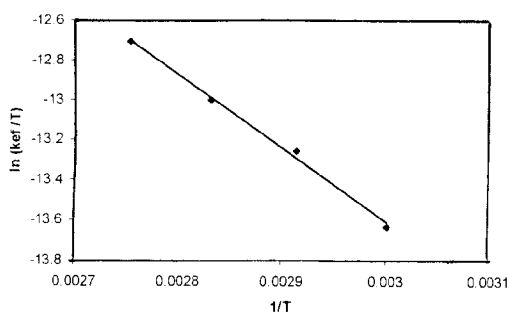

Fig. 3:   Plot of Eyring $\ln(k_{ef}/T)$ vs. 1/T.

Experimental

Titanium dioxide TiO_2 was used as a support. The BET specific surface area of sample, S, was higher than 500 m^2/g. In the preparation of the catalysts 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 potential of catalyst (5 wt % Fe_2O_3 on the surface of TiO_2) were studied for the reaction of isomerization of 3,4-dichloro-1-butene into 1,4-dichloro-2-butene in the temperature range of 60-90 °C. This reaction was investigated with 0.04 g catalyst (for the 5 wt % Fe_2O_3 on the surface of SiO_2 – 0.000036 mol Fe) in 0.3 ml (0.0028 mol) stirred 3,4-DCB-1. The following procedure was used to obtain catalytic data. An accurately weighed portion 0.04 g (3.6×10^{-5} mole Fe) of the catalyst sample was placed in a glass ampoule and 0.3-mL of freshly distilled 3,4-dichloro-1-butene was added into the ampoule. Then, the ampoule was sealed, and the reaction mixture was stirred under thermostatic conditions at temperatures varied from 60 to 90 °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. Five to eight ampoules were used to obtain one catalytic curve.

The analysis of products was carried out by gas-liquid chromatography. The major product of the reaction was *trans*-1,4-dichloro-2-butene; the amount of *cis*-1,4-dichloro-2-butene produced in the reaction was less than 2 %. Other products in the isomerization reaction were not detected. A typical compositional analysis of reaction with 0.04 g catalyst of 5 wt % Fe_2O_3 on the surface of TiO_2 at 90 °C being reported in Table-4.

It is known that in the heating of $FeCl_3$ in an oxygen flow or in the passing of water vapor over

Table-3: Direct, indirect, and effective enthalpy and entropy of activation for isomerization of 3,4-dichloro-1-butene to 1,4-dichloro-2-butene in the temperature range of 60-90°C.

ΔH_{ef}^* (kJ/mol)	ΔH_1^* (kJ/mol)	ΔH_{-1}^* (kJ/mol)	ΔS_{ef}^* $(kJ/mol.K)$	ΔS_1^* $(kJ/mol.K)$	ΔS_{-1}^* $(kJ/mol.K)$
30.56±3	30.41±3	34.07±3	-0.219±0.02	-0.222±0.02	-0.223±0.02

Table-4: Compositional analysis of reaction with 0.04 g catalyst of 5 wt % Fe_2O_3 on the surface of TiO_2 at 90 °C.

t (min)	Conversion of the reactant (%)
0	0
5	25
10	42
15	53
20	58
25	63
30	66
35	71
50	74

heated $FeCl_3$, the chloride is transferred into oxide (Fe_2O_3) according to the following reactions [11]:

$$2 \, FeCl_3 + 3/2 \, O_2 \longrightarrow Fe_2O_3 + 3 \, Cl_2$$
$$2 \, FeCl_3 + 3 \, H_2O \longrightarrow Fe_2O_3 + 6 \, HCl$$
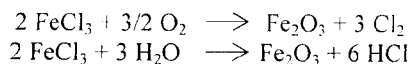
Conclusions

The catalyst containing Fe_2O_3 particles on the TiO_2 support was obtained using a simple procedure under mild conditions; its catalytic activity in the isomerization of 3,4-dichloro-1-butene into 1,4-dichloro-2-butene was comparable to or higher than that for the catalysts obtained by the conventional procedure.

References

1.   V. V. Smirnov, E. N. Golubeva and T. N. Rostovshchikova, *Kinetics and Catalysis*, **33**, 58 (1992).

2.   T. N. Rostovshchikova, V. V. Smirnov and E. V. Vovk, *Kinetics and Catalysis*, **33**, 682 (1992).

3.   T. N. Rostovshchikova, V. V. Smirnov and A. Yu, Bogomolov, *Vestnik Moskovskogo Universiteta, Seriya 2. Khimiya*, **36**, 145 (1995).

4.   T. N. Rostovshchikova, V. V. Smirnov and A. I. Kokorin, *Journal of Molecular Catalysis A: Chemical*, **129**, 141 (1998).

5.   T. N. Rostovshchikova, V. V. Smirnov, V. M. Kozhevin, D. A. Yavsin and S. A. Gurevich, *Kinetics and Catalysis*, **44** 555 (2003).

6.   C. Kurts, Y. Arita, W. Weiss, W. Ranke and R. Schlogl, *Topics in Catalysis.*, **14**, 111 (2001).

7.   T. N. Rostovshchikova, O. I. Kiseleva, G. Yu, Yurkov, *Vestnik Moskovskogo Universiteta., Seriya. 2. Khimiya.* **42**, 318 (2001).

8.   T. N. Rostovshchikova, V.V. Smirnov, M.V. Tsodikov, O. V. Bukhtenko, Y. V. Maksimov, O. I. Kiseleva and D. A. Pankratov, *Russian Chemical Bulletin International Education*, **54**, 1418 (2005).

9.   E. M. Asatryan, N. L. Saakyan, E. V. Golneva and G. T. Martirosyan, *Chemical Journal of Armenia*, **39**, 584 (1986).

10. S. Glasstone, K. J. Laidler and H. Eyring, The Theory of rate processes, New York: Mc Graw-Hill, (1941).

11. H. Remy, Textbook of Inorganic chemistry, Leipzig: Geest & Portig, (1949).