

The Kinetics of Double Bond Shift Isomerization of the Three Methylcyclohexenes and Methylenecyclohexane over γ -Alumina as a Catalyst

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The isomerization of 1-methylcyclohexene-1 (1MCH1), 3-methylcyclohexene-1 (3MCH1), 4-methylcyclohexene-1 (4MCH1), and methylenecyclohexane (MECH) over γ -alumina in 180°C in a batch reactor leads predominantly to double bond migration. The migration occurs stepwise according to the scheme: $\text{MECH} \rightleftharpoons \text{1MCH1} \rightleftharpoons \text{3MCH1} \rightleftharpoons \text{4MCH1}$. The rates are first order in the reactants. The overall relative rate constants are calculated. The composition of the equilibrium mixture of the four isomers at 180°C in the vapor phase consists of 73.4% 1MCH1, 10.7% 3MCH1, 14.1% 4MCH1, and 1.7% MECH.

INTRODUCTION

Isomerization of the three methylcyclohexenes and methylenecyclohexane leads to equilibrium mixtures in which each of the four compounds are present; the composition of these mixtures is defined by differences in their relative stability. This stability decreases according to the sequence: 1-methylcyclohexene-1 (1MCH1) \gg 4-methylcyclohexene-1 (4MCH1) $>$ 3-methylcyclohexene-1 (3MCH1) \gg methylenecyclohexane (MECH) (1, 2).

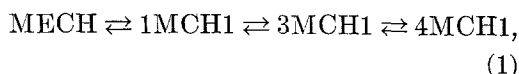
Nonbonded interactions and σ -bond stabilization energy account predominantly for the inequality in the relative stabilities of the endoisomers (1), the compound with the trisubstituted double bond being more stable than the compounds with the disubstituted double bonds. There is no clear explanation for the energetic preference of the methyl group for the 4- rather than the 3-position (3). In order to explain the difference in stability between 1MCH1 and MECH one has to look at the configuration of the ring. It then appears that the endo-

isomer has one less diaxial interaction between two H atoms than does the exo-isomer. Moreover, repulsions exist between the H atoms of the CH_2 group and the H atoms of the ring.

Equilibrium concentrations of the four isomers, at 25 (liquid phase) and 250°C (gas phase), are known from Herling *et al.* (4), while recently Yuïsha and co-workers (5) have published data concerning the temperature range from 0° to 380°C. However, the results of the two groups of investigators are not in full agreement with each other (Table 2).

Investigations made by Maurel *et al.* (6) present the reaction paths of the endoisomers only, without calculating the rate constants.

In this article, the reaction paths are presented for the isomerization of each of the four compounds over γ -alumina at 180°C. The pseudo-first-order relative rate constants are calculated for the scheme:



and the equilibrium composition of the reaction system is given.

EXPERIMENTAL METHODS

Materials. 1-Methylcyclohexene-1 (from Fluka, Germany) was purified from methylenecyclohexane by means of a spinning band distillation column. Methylenecyclohexane, 3-methylcyclohexene-1 (both from Fluka), and 4-methylcyclohexene-1 (from KEK, U. S. A.) were used without further purification; no impurities could be detected by gas-liquid chromatography.

The catalyst was γ -alumina (extrudates) supplied by Akzo, Amsterdam, type CK 300, 98.3% Al_2O_3 , with a surface area of 191 m^2/g and pore volume of 0.50 cm^3/g . After crushing the extrudates, the fraction with a particle size ranging from 0.2 to 0.4 mm was used.

Apparatus and procedures. The isomerization was performed in a batch reactor consisting of a stainless-steel cylinder with a capacity of 5 cm^3 . The cylinder was placed in a bath of fluidized corundum powder. Heat was supplied to the reactor, the heater being controlled by a West temperature controller. Three Chromel-Alumel thermocouples were inserted in the bath at different heights, and one thermocouple was placed into the reactor. The temperature constancy inside the reactor was better than 0.5°C. Liquid samples (250 μl) were injected and evaporated via a preheated section (120°C). The total pressure in the system was kept constant at 1 atm by supplying nitrogen gas, the pressure being measured by an AB pressure transducer from Tyco, U. S. A. All the tubes were maintained at a temperature of at least 120°C, to prevent condensation of the gases.

The gas mixtures were circulated by an electromagnetic pump. The connection between the reactor system and the gas chromatograph was provided by a gas sample valve, with a sample size of 0.25

cm^3 . A 2.0-g catalyst was used for carrying out the experiments. The catalyst, after being submitted to an initial deactivation by contacting it with the reactants at 180°C, was heated in the reactor at 500°C in vacuum. It was then contacted with an oxygen stream for 1.5 hr, after which a nitrogen stream was supplied for 1 hr. This was followed by overnight evacuation at 500°C. The catalyst was finally cooled to 180°C. By this pretreatment, a rather constant, moderate catalytic activity was obtained.

Analysis. A Hewlett-Packard gas chromatograph Model 5700 with a flame ionization detector was used for the analysis of the isomer mixtures. Two stainless-steel columns (3 mm, i.d.) were packed with chromosorb W. A. W., impregnated with 30 wt% of $\text{AgNO}_3/\text{glycol}$ (2:1) (7). A 0.75-m column was used for the separation of 1MCH1, MECH, and the sum of 3 and 4MCH1.

After the emergence of 1MCH1 from the column, 3 and 4MCH1 were isolated by means of a valve system and brought on to a 4-m column, in order to speed up the analysis (the average time of analysis was 110 min). The best resolution was obtained at a temperature of 30°C and with flow rates of nitrogen of 2.5 and 7.5 cm^3/min for the short and long column, respectively.

Because of the overlap of the 3 and 4MCH1 peaks, especially when the ratio of the two compounds differs greatly from 1, and also because of the overlap of the main peaks with peaks of by-products, which are formed during the catalytic experiment, calculations of the compositions of the isomer mixture were performed on a digital computer, making use of curve-fitting by nonlinear regression (8, 9).

RESULTS

Order of the reaction. In general it may be assumed that in our case double bond isomerization is governed by first-order

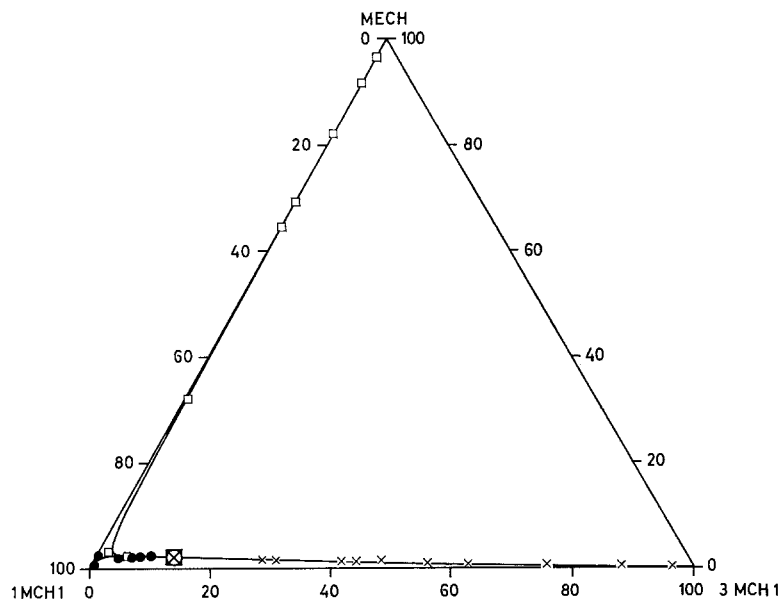


Fig. 1. Composition triangle for MECH, 1MCH1, and 3MCH1. (●) reaction path from 1MCH1, (×) reaction path from 3MCH1, (□) reaction path from MECH.

kinetics by analogy with the results found for *n*-butenes (10) and xylenes (11). Kubasov *et al.* (12) observed first-order behavior for the skeletal isomerization of cyclohexene, 1MCH1, and 4MCH1 over alumina.

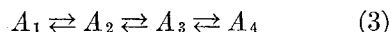
In order to verify this assumption for the methylenecyclohexenes and methylenecyclohexane, the method of Hightower and Hall (13) was adopted, using the relationship:

$$-\ln(X_e - X) = k't - \ln X_e \quad (2)$$

In this equation X and X_e represent the conversion of the starting isomer at time t and at equilibrium, respectively. This equation is strictly valid only for two components involved in a reversible first-order reaction, but it is a reasonable approximation for the four-component system at low conversions, if the three products are lumped together and treated as a single product. Furthermore, first-order behavior will only be found at low values of coverage of the adsorbed species, a condition which is fulfilled in our experiments, as appears from the slopes of the plots using Eq. (2).

For the three endo-isomers, a linear relationship is found up to at least 70% of the maximum conversion range, which points to a first-order reaction. The conversion of methylenecyclohexane, however, was too fast for drawing a reliable plot.

Reaction paths. Wei and Prater (14) have shown that heterogeneous catalytic reactions will be pseudo-first-order, if they are of the monomolecular Langmuir-Hinshelwood type (15). In that case the reaction rate equations for the scheme:



will have the form:

$$-\frac{da_i}{dt} = \phi \left[- \sum_{j \neq i} k_{ji} a_i + \sum_{j \neq i} k_{ij} a_j \right] \quad (i = 1, 2, 3, 4), \quad (4)$$

in which a_i is the mole fraction of species A_i and k_{ij} the pseudo-first-order rate constant for the reaction from the j th to the i th species. ϕ is a function of composition and time, and the same for all rate equations in the system.

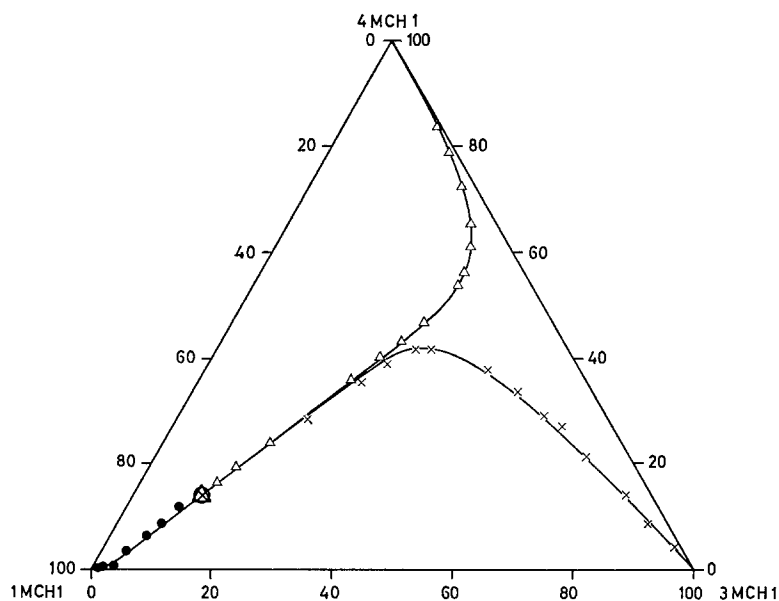


FIG. 2. Composition triangle for 1MCH1, 3MCH1, and 4MCH1. (●) reaction path from 1MCH1, (×) reaction path from 3MCH1, (Δ) reaction path from 4MCH1.

Assuming that the abovementioned conditions apply to the isomerization under investigation, Eq. (4) will describe the overall behavior of the reaction system.

The assumption for this scheme is made plausible in the discussion.

Because of the fact that in the succeeding experiments the activity of the catalyst

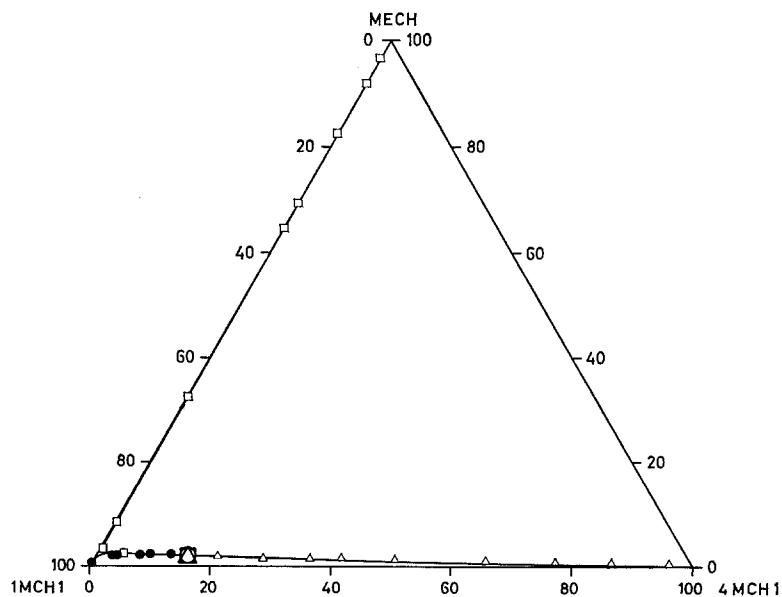


FIG. 3. Composition triangle for MECH, 1MCH1, and 4MCH1. (●) reaction path from 1MCH1, (Δ) reaction path from 4MCH1, (□) reaction path from MECH.

gradually decreased, it was desirable to carry out the calculations on the basis of composition sequences only, by eliminating the time from Eq. (4). Then a reaction path may be represented by a trajectory in a tetrahedron of which each vertex represents a pure isomer.

Figures 1-4 give the projections on the four composition triangles, which are the boundary planes of the tetrahedron. For clarity in presentation, many experimental points have been omitted especially in the region near the equilibrium point.

Calculations. In the calculation of the overall relative rate constants, all the results of the four different isomerizations were used. After the time was eliminated, Eq. (4) was numerically integrated by use of the method of Runge-Kutta (18). The desired parameters were found by curve-fitting, according to the procedure of Marquarte (9) (the rate of the thermal isomerization or catalytic isomerization by the wall of the reactor could be neglected). The results are given in Table 1.

Equilibrium measurements. Starting from each of the pure isomers, the same stable composition was found (Table 2), confirming that thermodynamic equilibrium was attained. The mean values of the equilibrium concentrations were calculated and are given in the sixth column of Table 2. The deviations were calculated from the deviations of the mean values, for all the separate measurements of the equilibrium composition.

From the kinetic data k_{ij} in Table 1, the equilibrium constants $K (=k_{ij}/k_{ji})$ for each step can be calculated. These K values appear to be in perfect accordance with the equilibrium K values which are calculated from the equilibrium composition (Tables 2 and 3).

DISCUSSION

The mechanism of olefin isomerization over activated γ -alumina to 500°C is still not fully clear. Kubasov *et al.* (12) concluded that the adsorption of unsaturated compounds on γ -alumina was a result of an

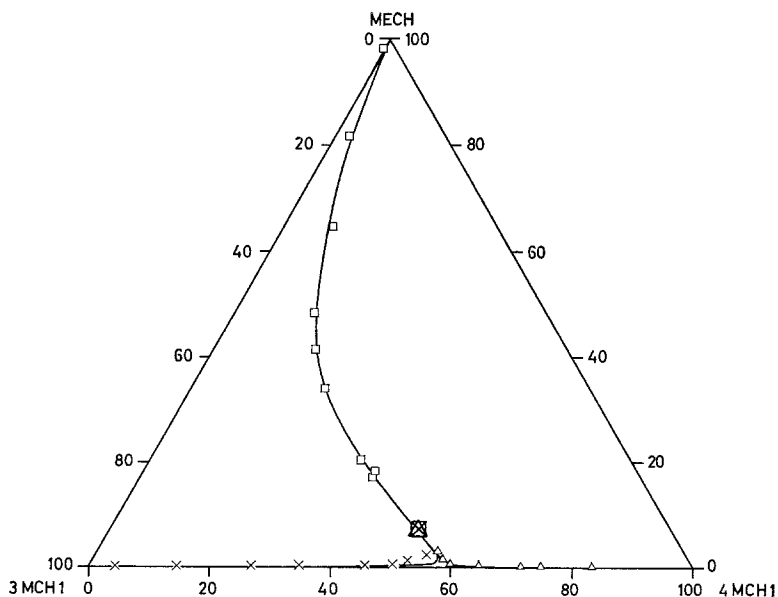


Fig. 4. Composition triangle for MECH, 3MCH1, and 4MCH1. (×) reaction path from 3MCH1, (Δ) reaction path from 4MCH1, (□) reaction path from MECH.

TABLE 1

Overall Relative Rate Constants for the Isomerization of the Methylcyclohexenes and Methylene-cyclohexane over γ -Alumina at 180°C, and 1 atm Total Pressure

A_i	$A_i \xrightarrow{k_{ji}} A_j$			
	1MCH1	3MCH1	4MCH1	MECH
1MCH1 ^a	—	9	—	24
3MCH1 ^a	59	—	188	—
4MCH1 ^a	—	154	—	—
MECH ^b	1000 ^c	—	—	—

^a Initial partial pressure of 0.14 atm.

^b Initial pressure of 0.12 atm.

^c Arbitrarily chosen.

interaction of the double bond with low-coordinated surface aluminium ions. This interaction, in the precatalytic state (80°C), was possible only for an edgewise orientation of the cyclene on double (and triple) vacancies. This agrees with Hightower and Hall's idea, that the migration of the double bond is an intramolecular process, whereby the olefine is draped over a surface oxide ion (16).

Corado *et al.* (17) suggested two types of sites. The A site is characterized by a high specific acitivity for the double bond shift. It should not contain reactive hydrogen and must therefore catalyze an intramolecular hydrogen shift. This site leads to the formation of an "oxygen"-containing compound, which poisons the site and

TABLE 3

Equilibrium Constants, K , Calculated from the Kinetic Data k_{ij} and from the Mean Values of the Equilibrium Concentrations

K	From k_i/k_j	From the equilibrium concentrations
[MECH]/[1MCH1]	0.024	0.023
[3MCH1]/[1MCH1]	0.15	0.15
[3MCH1]/[4MCH1]	0.82	0.76

eliminates it as an active site for the shift. Type B sites exhibit no oxidizing properties and are therefore not eliminated by self-poisoning. They have reactive hydrogen available and the double bond shift occurs with an intermolecular hydrogen shift under participation of surface hydroxyls. The B sites may be specified to consist of a basic oxygen, an acidic part, and a hydroxyl group. The type A sites correspond with the sites mentioned by Hightower and Hall. Since the self-poisoning does not occur at lower temperatures, Hightower and Hall did not observe deactivation of the catalyst. However, at higher temperatures, the hydrogen transfer should change from intramolecular to intermolecular during the reaction. At the temperature of the isomerization of the methylcyclohexenes and methylenecyclohexane (180°C), one can suppose that type B sites are predominantly active. Nevertheless, the same considerations are valid, on the grounds, of which the

TABLE 2

Equilibrium Composition of the Isomeric Methylcyclohexenes and Methylene-cyclohexane at 180°C and 1 atm^a

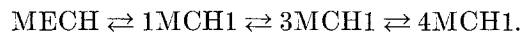
Isomer	Starting isomer				Mean values	Herling <i>et al.</i> (4)	Yuïsha <i>et al.</i> (5)
	1MCH1	3MCH1	4MCH1	MECH			
1MCH1	73.54 ± 1.48	73.19 ± 0.48	73.27 ± 0.41	73.94 ± 0.54	73.39 ± 0.73	70.65	73.17
3MCH1	10.55 ± 0.50	10.72 ± 0.33	10.74 ± 0.02	10.71 ± 0.22	10.67 ± 0.27	12.39	10.10
4MCH1	14.30 ± 1.12	14.54 ± 0.41	13.98 ± 1.66	13.68 ± 0.30	14.11 ± 0.87	15.44	15.11
MECH	1.62 ± 0.12	1.54 ± 0.07	2.01 ± 0.17	1.67 ± 0.07	1.71 ± 0.11	1.52	1.62

^a Values given as mole percentages.

direct isomerization of MECH into 3 or 4MCH1 has to be excluded. Experimental indications for these conclusions are found in the selectivity diagrams (Figs. 1-4).

From Fig. 2, the composition triangle of 1MCH1, 3MCH1, and 4MCH1, it appears that the asymptotic courses of the paths from 4MCH1 and 1MCH1 do exclude the direct conversion between 1 and 4MCH1, just as was found by Maurel *et al.* (6). From Fig. 1 one can conclude in the same way that there is no direct conversion between MECH and 3MCH1.

In view of the above, the assumption for the overall reaction model of the isomerization is:



Catalytic isomerization takes place via adsorption, after which the conversion proceeds by stepwise surface reactions which are rate determining.

For calculating the overall relative rate constants, the assumption was made that the system is pseudo-first-order and that the function ϕ is the same for each of the Eqs. (4). In spite of the slight deactivation during successive runs, whereby the number of active sites decreases, the pseudo-monomolecular model is still applicable, assuming that the deactivation reduces the various rate constants k_{ij} by a similar factor.

The straight lines obtained by applying Hightower and Hall's method are further experimental indications pointing to first-order behavior.

Using only one path, quite accurately calculated compositions are obtained in the neighborhood of the starting isomer, but the agreement for compositions away from this region can be very poor. By using all the compositions of the four different paths together, rate constants are found which are sufficiently accurate to

calculate a composition everywhere in the reaction simplex.

The reliability of the overall relative rate constants depends on the accuracy of the analysis of the isomer mixtures. Most of the concentrations could be determined with an accuracy of 2-4%, by means of the computer procedures. However, the error made by the estimation of the composition of the mixtures obtained from the isomerization of 4MCH1 were large at the beginning (up to 10%) because of the large differences in the amounts of 4 and 3MCH1, and due to the fact that these two compounds are not completely separated in the chromatograms.

From the data of Herling *et al.* (4) and Yuïsha *et al.* (5), the equilibrium composition for the isomerization at 180°C are calculated and, together with our experimental results, are reported in the last two columns of Table 2. Our data are in better accordance with those of Yuïsha *et al.* than with the data of Herling *et al.* Probably our methods developed for analyzing the experimental data provide a better accuracy.

The fact that the equilibrium constants for each step: $A_i \rightleftharpoons A_j$, as calculated from the kinetic parameters, are in such a good agreement with the K values observed, gives more support to the scheme proposed.

Finally we conclude that a time-elimination procedure is a suitable method in cases where the catalyst varies in activity from one experiment to another.

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