

Double-Bond Isomerization of the Methylcyclohexenes and Methylene cyclohexane over γ -Alumina

M. PEEREBOOM

Laboratory of Inorganic and Physical Chemistry, Delft University of Technology,
P.O. Box 5045, 2600 GA Delft, The Netherlands

Received September 7, 1983; revised January 23, 1984

Relative pseudo-first-order rate constants are calculated for the double bond shift isomerization of the three methylcyclohexenes and methylenecyclohexane over γ -alumina in a batch reactor in the temperature range 413–523 K. Skeletal isomerization can be prevented by pretreatment of the catalyst with cycloalkenes. Reaction paths in the selectivity diagrams, as well as low-conversion data obtained in a microreactor, are consistent with the isomerization reaction being a series reaction. Probably, at least the isomerization of the endocyclic isomers proceeds via a π -allyl mechanism.

INTRODUCTION

The isomerization reactions of the methylcyclohexenes and methylenecyclohexane are of interest in connection with the study of the double bond shift isomerization and the skeletal rearrangement of cycloolefins. Equilibrations carried out in the liquid phase using relatively mild homogeneous acid catalysts (e.g., *p*-toluenesulfonic acid in acetic acid), revealed a migration of the double bond between the exo and 1-endo position only (1, 2). In the gas phase, by using activated γ -alumina, double bond isomerization leads to equilibrium mixtures in which each of the four compounds, 1-, 3-, and 4-methylcyclohexene (1MCH, 3MCH, and 4MCH, respectively) and methylenecyclohexane (MECH) were present (3). The amount of skeletal isomers is very small during experiments carried out below 493 K, but at higher temperatures an increase of mainly ethylcyclopentenes (ECP) and dimethylcyclopentenes (DMCP) was demonstrated (4).

According to Kubasov *et al.* (4), adsorbed cycloalkenes are edgewise oriented on the surfaces of alumina in the precatalytic state. Their results were in agreement with the studies of Hightower and Hall (5) on small alkenes at temperatures of less

than 375 K. Sites mentioned by Hightower and Hall correspond with the A-type sites suggested by Corado *et al.* (6). These A-sites catalyze an intramolecular hydrogen shift, but are blocked by self-poisoning at higher temperatures. Type-B sites involve Lewis acid sites and remain active at all temperatures leading to an intermolecular hydrogen shift. From a study on the isomerization of 3-methylcyclopentene, Irvine *et al.* (7) conclude that double bond migration occurs in the endo isomer predominantly via π -allyl intermediates on Lewis acid sites, whereas double bond migration in the exo isomer occurs via carbenium ion intermediates on Brønsted acid centres. Similar results can be derived from the experimental work of Carleton *et al.* (8) on reactions of alkenes on Ga_2O_3 . These investigators show that rapid isomerization of methylenecyclopentane to 1-methylcyclopentene can occur where the π -allyl mechanism does not operate in a simultaneous double bond migration around the ring.

The purpose of the present work was to obtain sets of relative reaction rate constants at different temperatures and to relate them to a kinetic scheme that can be discussed with respect to the underlying reaction mechanism. As support to the study of this complex reaction system, the micro-

catalytic pulse technique is applied for the investigation of the selectivity behavior of the catalyst at low conversions.

EXPERIMENTAL

Materials, batch reactor, procedures, and analysis used for the investigation of the kinetics of the isomerization were described in a previous paper (3).

The microreactor was of stainless steel with an internal volume of 10 cm³. Heat was supplied by a small block furnace, keeping the reaction temperature constant within 0.5°C. The catalyst temperature was measured with a Chromel–Alumel thermocouple. At all reaction temperatures, pure nitrogen carrier gas, dried by a molecular sieve, flowed over the catalyst at 11.3 cm³ (stp) min⁻¹ and 1 atm pressure. By way of comparison with the experiments in the batch reactor, the microreactor was charged with 2.0 g catalyst (0.2–0.4 mm), held in place with plugs of glass wool, while liquid samples of 250 μl were introduced into the nitrogen stream ahead of the catalyst. Products from each slug were collected in a cold trap (CO₂/acetone), after which samples of the condensate were injected onto the chromatographic column.

For both a fresh catalyst and a catalyst initially deactivated with reactant, the mode of treatment was similar to the one used in the batch reactor experiments. By means of successive pulses, selectivity determinations were made on these two kinds of catalyst.

RESULTS

Batch Reactor

Starting from each of the pure isomers, equilibrations were carried out at temperatures of 413, 433, 453, 473, 493, and 523 K. The method of Hightower and Hall (9) was applied to the conversion data, yielding linear relationships up to at least 70% for the endo isomers. Under the experimental conditions employed, these results indicate a first-order behavior of the reaction system.

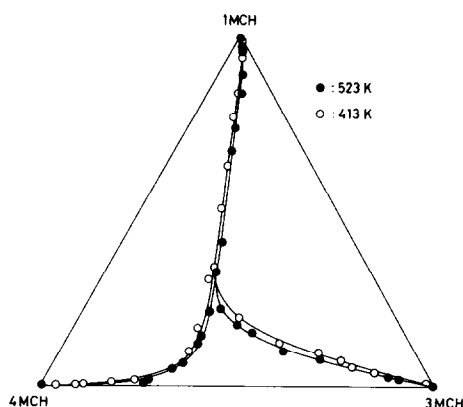


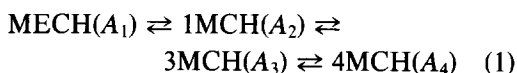
FIG. 1. Plot of the approach to the equilibrium composition of 1MCH, 3MCH, and 4MCH, at the lowest (413 K) and highest (523 K) reaction temperature. The calculated reaction paths are represented by the solid lines.

The exo isomer (MECH) reacted too fast to obtain reliable conclusions.

The selectivity behavior of the catalyst appears from the particular composition sequences that are produced from a given initial composition. These sequences constitute reaction paths into the interior of a tetrahedron of which each vertex represents a pure isomer. In order to survey the results, use is made of the projections of the reaction paths, obtained by normalizing, onto each of the faces of the tetrahedron.

At all reaction temperatures, asymptotic courses of the paths from 4MCH to 1MCH in the composition triangle of 1MCH, 3MCH, and 4MCH and of MECH to 3MCH in the composition triangle of MECH, 1MCH, and 3MCH occur (Fig. 1).

As proposed previously (3), the overall reaction model is probably represented by



Assuming Langmuir-type adsorption, the kinetic rate equations for the pseudo-monomolecular reaction system are given by the linear differential equations (10)

$$-d a_i/d\tau = - \sum_{j \neq i}^j k_{ji} a_i + \sum_{i \neq j}^i k_{ij} a_j$$

$$(i = 1, 2, 3, 4) \quad (2)$$

a_i is the mole fraction of species A_i , k_{ij} is the rate constant for the conversion of the j th to the i th species, and τ is a fictitious time-scale.

After elimination of the time, the relative pseudo-first-order rate constants k_{ij} are calculated from Eq. (2), optimization procedures being used. At a specific temperature, the calculations were carried out using all the data of the four different isomerization paths together. Values of the relative rate constants (with an accuracy of about 10%) are reported in Table 1.

Although each reaction path has been obtained by successive runs using a catalyst with varying activity, experimental and calculated points are in good agreement (e.g., Fig. 1). It appears that all reactants display a similar adsorption behavior. By comparison, k -values have been calculated for schemes with 8 parameters ($A_1 \rightleftharpoons A_2 \rightleftharpoons A_3 \rightleftharpoons A_4 \rightleftharpoons A_1$) and 12 parameters (a scheme in which all interchanges are possible). Rate constants for steps not involved in the linear model are some orders of magnitude less (Table 2). Moreover, only equilibrium calculations based on the kinetic data of scheme (1) are in a very good agreement at all temperatures with equilibrium compositions experimentally measured (Table 3) and are in accordance with values calculated using molecular mechanics (11). These findings give supplementary support for the proposed linear scheme; thus the schemes with 8 and 12 parameters are now left out of consideration.

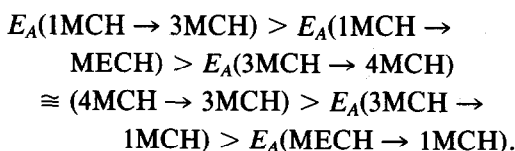
From the data of Table 1 it appears that the temperature dependence of the relative rate constants is rather small. From the Arrhenius plots (Fig. 2) values of the differences in activation energies of reaction 32 and reaction $ij(E'_A)$ and the ratios of the frequency factors have been calculated and are reported in Table 4. The order of magnitude of the differences between the values

TABLE 1
Relative Overall Rate Constants ($k_{32} = 1$)

Temperature (K)	k_{12}	k_{21}	k_{23}	k_{34}	k_{43}
413	2.05	103	8.07	24.3	19.1
433	2.58	121	6.95	22.9	18.6
453	2.70	110	6.51	20.8	16.9
473	1.48	56	5.88	20.8	16.5
493	2.28	86	5.25	20.8	17.2
523	1.84	53	5.09	18.1	14.6

of E'_A is in agreement with those obtained by Kubasov *et al.* (4) for conversion data of 1MCH and 4MCH in a pulse reactor.

On account of these values the following sequence of the energies of activation can be given



Microreactor

Using the slug injection technique, limited quantities of the pure reactant have been brought onto the catalyst. The first experiments are carried out on the activated fresh catalyst, not pretreated with cyclene. After 3–5 pulses, a constant activity of the catalyst is achieved. The resulting gas mix-

TABLE 2
Calculated Relative Overall Rate Constants for Various Reaction Schemes at 433 K ($k_{21} = 1$)

k_{ij}	6 parameters	8 parameters	12 parameters
k_{12}	2.1×10^{-2}	2.5×10^{-2}	2.1×10^{-2}
k_{32}	8.3×10^{-3}	10.3×10^{-3}	8.5×10^{-3}
k_{23}	5.8×10^{-2}	5.6×10^{-2}	5.8×10^{-2}
k_{34}	1.5×10^{-1}	2.2×10^{-1}	2.0×10^{-1}
k_{43}	1.9×10^{-1}	1.8×10^{-1}	1.6×10^{-1}
k_{14}		1.5×10^{-5}	2.4×10^{-3}
k_{41}		2.3×10^{-6}	1.1×10^{-4}
k_{24}			1.4×10^{-4}
k_{42}			3.7×10^{-4}
k_{31}			4.2×10^{-3}
k_{13}			7.1×10^{-5}

TABLE 3

Calculated and Experimentally Measured Values of the Equilibrium Compositions

	413 K		433 K		453 K	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
MECH	1.5	1.5	1.5	1.6	1.6	1.8
1MCH	77.1	76.9	74.4	74.5	73.4	73.2
3MCH	8.9	9.5	10.5	10.7	10.8	11.2
4MCH	12.5	12.1	13.7	13.2	14.3	13.8
	473 K		493 K		523 K	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
MECH	1.5	1.9	1.7	1.8	1.9	2.4
1MCH	71.1	70.9	69.5	69.1	68.0	67.8
3MCH	11.4	12.1	12.2	13.2	13.6	13.3
4MCH	16.0	15.2	16.6	15.9	16.6	16.6

tures show only small differences between the mutual ratios of the methylcyclohexenes. Characteristic is the presence of a number of skeletal isomers and products of disproportionation. These species are mainly 1-ethylcyclopentene (1-ECP), 1,2-dimethylcyclopentene (1,2-DMCP), methylcyclohexane, and toluene. At the highest reaction temperature, the amount of by-products does not exceed 6% on the fresh catalyst and 2% on the catalyst with a constant activity. These figures are obvious smaller than those of Kubasov *et al.* (12)

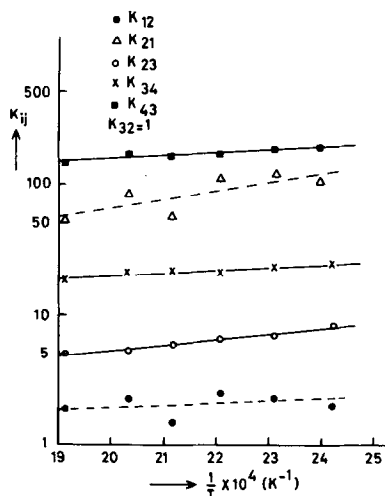


Fig. 2. Arrhenius plot of relative rate constants.

TABLE 4

Calculated Differences in Activation Energies of Reaction 32 and Reaction *ij* and Ratios of the Frequency Factors

k_{ij}	k_{ij}^0/k_{32}^0	E_A^i (kJ mol ⁻¹)
k_{12}	0.8	3.6
k_{21}	3.5	12.2
k_{23}	0.8	7.8
k_{34}	7.0	4.2
k_{43}	6.2	3.9

but are in accordance with the results of Herling *et al.* (13). However, we have been successful in suppressing the formation of skeletal isomers altogether, in experiments carried out with a catalyst pretreated with cycloalkene. In the temperature range studied and using varying flow rates, conversions based on 4MCH did not show the presence of MECH, while, contrary to the findings of Kubasov *et al.*, in all experiments the presence of 3MCH could be demonstrated (Table 5).

DISCUSSION

The assumption can be made that skeletal isomerization of cyclenes over alumina depends on the presence of strong acid sites (double and triple vacancies of the layer of oxygen ions of the regular lattice), while double bond shift isomerization takes place on weak acid sites (single vacant sites or

TABLE 5

Conversion Data in a Microreactor for the Catalyst Pretreated with Cyclene

Starting isomer	Composition of the reaction mixture			
	MECH	1MCH	3MCH	4MCH
MECH	63.49	35.93	0.44	0.14
1MCH	1.19	98.23	0.40	0.18
3MCH	0.07	2.92	94.36	2.65
4MCH	—	0.45	2.26	97.29

Note. Reaction temperature 433 K. Contact time 50 s.

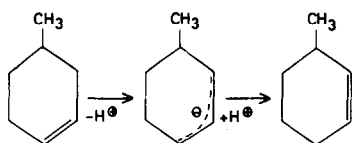


FIG. 3. Isomerization of 4MCH via an allyl carbanion.

Brønsted acid sites). In view of the composition of the reaction mixtures obtained with the microreactor experiments, skeletal isomerization may proceed by means of the mechanism proposed by Kubasov *et al.* (4), assuming the edgewise orientation of the cyclene on multiple vacancies. However, because of the presence of 3MCH, shown in all our experiments, their reaction scheme including both skeletal and double bond isomers, must be incorrect. Probably, as a result of their analytical conditions (high column temperature and high carrier gas velocity), a separation between 3MCH and 4MCH is impossible.

For double bond shift isomerization, carbenium ion mechanism have been proposed (7), the proton coming from Brønsted acid sites. When considering the calcining temperature of 773 K, the number of hydroxyl groups on the catalyst surface is almost negligible and thus a Brønsted mechanism under these conditions is not very likely (14). Protons provided by adsorption of cyclene fragments on the dehydrated surface seem possible (15).

From the microreactor experiments it appears that the catalyst pretreated with cyclene eliminates the sites responsible for skeletal rearrangement, leaving only the weak Lewis acid sites. These findings agree with the idea of Corado *et al.* (6) concern-

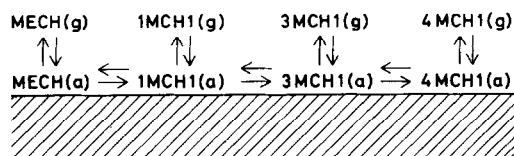


FIG. 4. Reaction scheme for the isomerization of the methylcyclohexenes and methylenecyclohexane over alumina.

ing the A- and B-type sites. Double bond shift isomerization should then occur by interaction of the double bond with an exposed Al^{3+} -ion and a basic oxygen ion, forming allylic carbanion-like intermediates.

Similar to Irvine *et al.* (7), in view of their H_2S poisoning experiments, we propose a π -allylic mechanism for the double bond shift isomerization of the endocyclic isomers (Fig. 3). The very fast reaction of MECH may proceed by a proton-donating mechanism, favored because of the involvement of a tertiary carbenium ion (8, 15).

In conclusion, the considerations mentioned above, together with the product distributions obtained in the microreactor experiments and the courses of the reaction paths in the selectivity diagrams, are in favor of a stepwise, linear reaction scheme as previously indicated (Fig. 4).

ACKNOWLEDGMENTS

The author is indebted to Professor J. L. Meijering for helpful discussions and to Mr. B. Sonnevile for performing the experiments.

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