

The Selectivity in Ring Opening of Cyclohexane and Methylcyclopentane over a Nickel-Alumina Catalyst

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Ring opening of cyclohexane and methylcyclopentane (MCP) catalyzed by a nickel-alumina catalyst was investigated at a hydrogen pressure of 10 atm, in the temperature range from 230 to 320°C. MCP can react at a temperature some 50°C lower than cyclohexane. At lower temperatures, the major products of either reaction are hexane isomers which consist of *n*-hexane (HEX), 2-methylpentane (2MP), and 3-methylpentane (3MP). The composition of hexane isomers obtained from cyclohexane depends on the reaction temperature, and the relative molar proportions can be expressed as HEX:2MP:3MP = 2-6:1:1. The composition of hexane isomers obtained from MCP is almost unchanged over the temperature range and expressed as HEX:2MP:3MP = 1:5:5. It is found that ring opening of cyclohexane proceeds along two different paths: (a) isomerization to MCP with subsequent conversion to hexane isomers, (b) direct opening of the cyclohexane ring to form *n*-hexane. The difference in reactivities between cyclohexane and MCP is discussed in terms of the specific modes of their adsorption on the catalyst.

INTRODUCTION

Catalytic hydrocracking of pure naphthenes have been investigated in some detail over bifunctional metal-acidic oxide catalyst. The reactions of a number of cyclohexenes over a nickel sulfide on silica-alumina catalyst have been investigated by Egan *et al.* (1). They have shown that isobutane and cycloparaffins containing four carbon atoms less than the original cycloparaffin were formed as principal products by paring reaction and very little ring cleavage occurred.

The reactivities of cycloparaffins have been studied over metal or metal-supported catalysts. Hydrogenolysis of a cyclic C-C bond become more difficult with an increase of the ring size and the number of substituents (2).

Kochloeff and Bazant (3) have investigated hydrogenolysis of a series of alkyl-

cyclohexanes over a nickel-alumina catalyst and have shown that methyl groups were successively removed from alkyl side chain without ring cleavage. It has been also shown in our previous study (4) on hydrocracking of isopropylcyclohexane that hydrodemethylation of isopropyl side chain proceeded predominantly over a 46% molybdena-alumina catalyst reduced with H₂ at 550°C.

Hydrocracking of cyclohexane has been investigated by use of nickel-silica-alumina (5), zeolite (6, 7), and nickel (8) catalysts, but very little attention has been paid to the mechanism of direct opening of the cyclohexane ring. The fundamental study for ring opening of cyclohexane appears to provide much information for investigation of practical catalytic hydrocracking.

In the present study, the reactivities and selectivities for ring opening of cyclo-

hexane and methylcyclopentane were investigated over a nickel-alumina catalyst on which hydrogenolysis of a series of paraffinic hydrocarbons has been studied recently in this laboratory (9, 10).

EXPERIMENTAL METHODS

Materials

Methylcyclopentane of extra-pure-reagent grade was purified by distillation, and the sample was determined by gas chromatography to be of 99.98% purity. Cyclohexane (100.0% purity) of commercial reagent grade was used without further purification.

Catalyst

The nickel catalyst used in the present study contained 30 wt% NiO and was prepared from nickel nitrate precipitated on alumina. The alumina used as the support was the Ketjen high-purity alumina (227 m²/g surface area). After impregnation of alumina with a nickel nitrate solution, the catalyst was calcined in air at 450°C for 24 hr.

Apparatus and Experimental Procedure

The catalyst was supported inside a 14-mm i.d. by 600-mm long stainless steel tube. The dead space above and below the catalyst bed was packed with stainless steel beads. The hydrocarbon feed rates were measured by means of a microfeed pump (Tamaseiki CO.). The effluent from the reaction tube was introduced into a pressure separator and the uncondensed gas was passed through a pressure controller and discharged through a wet gas meter. A more complete description of the reactor and other equipment has been given elsewhere (4, 9).

In each experiment was used a 5 ml portion of nickel-alumina catalyst (20–50 mesh), which was reduced immediately before use with hydrogen at 450°C for 12

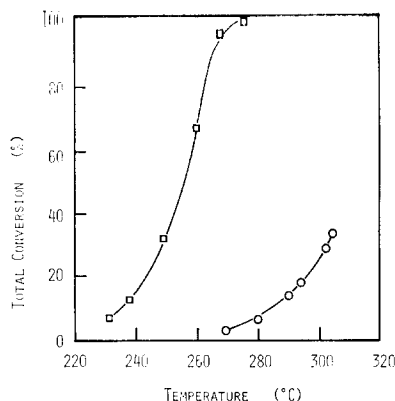


FIG. 1. Hydrogenolysis of cyclohexane and MCP. Hydrogen pressure, 10 atm; LHSV, 1.2 hr⁻¹; hydrogen flow rate, 1.80 mol/hr; H₂/HC (mol/mol): 33.0 (cyclohexane), 34.4 (MCP); (○) cyclohexane; (□) MCP.

hr under atmospheric pressure directly in the flow apparatus.

The reactions were carried out at a hydrogen pressure of 10 atm, in the temperature range from 230 to 320°C.

Analytical Method

A portion of the product mixture was introduced in gaseous state to an analytical unit and analyzed by means of a Hitachi Model 023 gas chromatograph with flame-ionization detectors using a squalane-coated alumina column (10 m × 2.0 mm) and a squalane capillary column (90 m × 0.25 mm). The peak areas were measured with a Takeda Model TR-2215 electronic integrator.

RESULTS AND DISCUSSION

The reactivities of cyclohexane and methylcyclopentane (MCP) were compared on the basis of the relations between the extent of conversion of the parent hydrocarbon and the reaction temperature. Experimental results are given in Fig. 1, which shows that MCP has much higher reactivity than cyclohexane has; the former reacts at a temperature some 50°C lower than the latter.

TABLE 1
Product Distribution from Hydrogenolysis
of Cyclohexane

Temperature (°C)	269.3	280.0	290.1	293.7	304.4
Total conversion (%)	3.23	6.53	14.01	18.21	33.98
Percentage products (100 mol/total moles of products)					
Methane	22.0	32.5	41.8	46.3	54.1
Ethane	3.3	2.6	2.0	2.0	2.0
Propane	0.5	0.8	1.3	1.5	2.4
Isobutane	—	0.1	0.3	0.3	0.5
Butane	4.0	4.2	4.8	5.1	6.2
Isopentane	1.2	1.8	2.4	2.6	3.0
Pentane	7.8	9.8	11.3	11.5	11.6
Hexanes	46.4	40.8	31.1	26.8	18.0
MCP	14.9	7.2	4.5	3.2	1.6
Benzene	—	0.3	0.6	0.6	0.5
Hexane composition (mol%)					
HEX	77.6	70.4	63.8	61.3	57.0
2MP	9.2	14.2	18.9	20.5	22.8
3MP	13.2	15.4	17.6	18.2	20.1

Reactions of Cyclohexane

The distribution of the reaction products of cyclohexane is shown in Table 1. The data were obtained over the temperature range of 269–304°C. The main products at 269°C are hexanes. Methane, ethane,

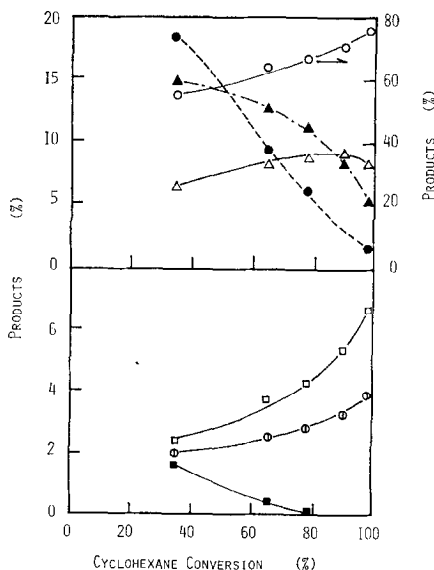


FIG. 2. Effect of extent of reaction on the product distribution for hydrogenolysis of cyclohexane. Temperature, 304°C; LHSV, 0.3–2.8 hr⁻¹; (○) methane; (⊙) ethane; (□) propane; (△) butanes; (▲) pentanes; (●) hexanes; (■) MCP.

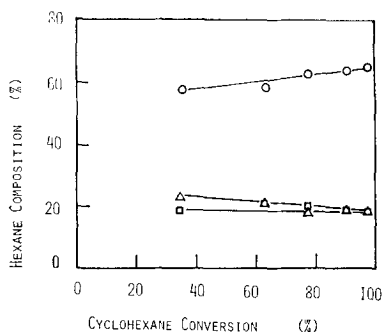


FIG. 3. Effect of extent of reaction on the hexane composition for hydrogenolysis of cyclohexane. Temperature, 304°C; LHSV, 0.3–2.8 hr⁻¹; (○) HEX; (△) 2MP; (□) 3MP.

propane, butanes, pentanes, and MCP appear also in the product. With an increase in the reaction temperature, the percentage of methane increases, while those of hexanes and MCP decrease. Very small amount of benzene is also observed at higher temperatures.

These results suggest that at lower temperatures the ring opening proceeds in the earlier stage of the reaction, while the subsequent cracking of the ring-opening products occurs significantly only at higher temperatures.

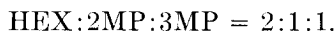
The composition of hexane isomers obtained at each reaction temperature is also given in Table 1. With an increase in the temperature, the ratio of *n*-hexane (HEX) to total hexanes decreases and those of 2-methylpentane (2MP) and of 3-methylpentane (3MP) increase, while the value of 2MP/3MP is almost independent of temperature. A possible explanation for these results is that the reaction mechanism of ring opening of cyclohexane to HEX is different from the mechanism of 2MP and 3MP formation.

The relationship between the distribution of products and the extent of reaction were studied. The results are given in Figs. 2 and 3. Data were obtained under following conditions: 304°C, 10 atm, 33.0 mol of hydrogen/mol of cyclohexane. The liquid hourly space velocity (LHSV) was

varied from 0.3 to 2.8 hr⁻¹ by changing the feed rate resulted in cyclohexane conversion from 27 to 98%.

Figure 2 shows that the percentages of methane and butanes increase, and those of hexanes and pentanes decrease with an increase in the extent of conversion.

The composition of hexane isomers at each extent of conversion is shown in Fig. 3. It is apparent that hexanes are produced in a constant composition over a very wide conversion range. The relative molar proportions are fairly well expressed as



As shown in our previous paper (10), the three hexanes are almost equivalent in reactivity for hydrogenolysis under the same conditions as those used in the present study. Therefore, a constant composition of hexane isomers will be maintained, regardless of the extent of hydrogenolysis.

Reactions of MCP

The distribution of each product from the reaction of MCP is given in Table 2. Data were obtained over the temperature range of 231–275°C. Hexanes are predominantly produced at lower temperatures. The percentages of methane and

TABLE 2

Product Distribution from Hydrogenolysis of MCP

Temperature (°C)	231.2	238.3	249.3	260.5	274.6
Total conversion (%)	6.5	12.0	32.2	67.4	99.5
Percentage products (100 mol/total moles of products)					
Methane	11.4	15.2	20.0	27.9	46.6
Ethane	0.9	0.6	0.7	0.7	1.1
Propane	0.5	0.3	0.2	0.2	1.0
Isobutane	—	0.1	0.3	0.5	1.4
Butane	0.1	0.3	0.5	1.1	3.4
Isopentane	5.3	5.7	6.6	8.0	10.8
Pentane	0.7	1.1	2.0	4.0	7.6
Hexanes	81.0	76.7	69.7	57.5	28.1
Hexane composition (mol%)					
HEX	12.5	9.6	8.8	8.9	10.0
2MP	46.2	47.1	46.5	45.6	43.6
3MP	41.3	43.4	44.8	45.5	46.2

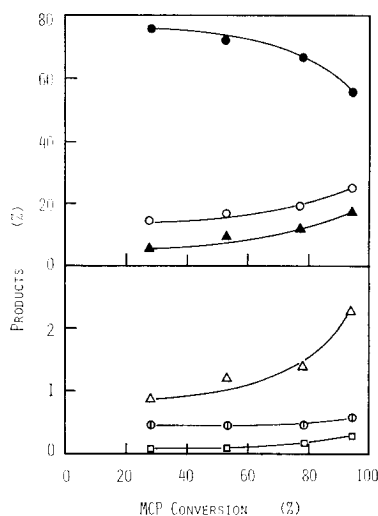
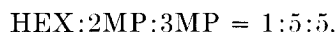


FIG. 4. Effect of extent of reaction on the product distribution for hydrogenolysis of MCP. Temperature, 260°C; LHSV, 0.35–2.5 hr⁻¹; (○) methane; (◐) ethane; (◑) propane; (△) butanes; (▲) pentanes; (●) hexanes.

pentanes increase with temperature. The formation of cyclohexane, benzene, or cyclopentane is not observed over the entire temperature range. The composition of hexane isomers is almost independent of temperature and the relative molar proportions are approximately expressed as



The ratio of HEX to total hexanes in the reaction of MCP is much lower than the ratio in the reaction of cyclohexane, while the values of 2MP/3MP are almost equal in both reactions.

The relationships between the distribution of products and the extent of reaction were investigated at 260°C, with 33.4 mol of hydrogen/mol of MCP. Figure 4 shows that the percentage of hexane decreases continuously, while those of methane, pentanes, and butanes increase with an increase in the extent of conversion.

Figure 5 shows that the composition of hexane isomers is almost independent of the extent of conversion.

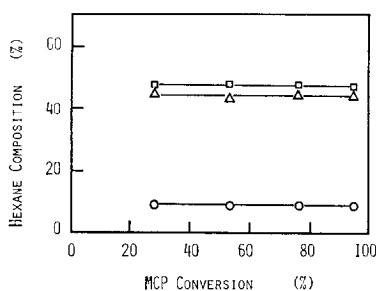


Fig. 5. Effect of extent of reaction on the hexane composition for hydrogenolysis of MCP. Temperature, 260°C; LHSV, 0.35–2.5 hr⁻¹; (○) HEX; (△) 2MP; (□) 3MP.

Reaction Paths in Ring Opening of Cyclohexane

A reaction scheme can be discussed in view of the experimental facts that significant amounts of MCP present in the product of the reaction of cyclohexane and that the value of 2MP/3MP from cyclohexane is equal to the value from MCP. It seems reasonable to suppose that 2MP and 3MP are formed by ring opening of MCP which arises from the isomerization of cyclohexane. The high ratio of HEX to total hexanes in the reaction of cyclohexane also suggests the possibility of direct opening of the cyclohexane ring. A reaction scheme to account for the observed data is given in Fig. 6, which includes two parallel reaction paths for ring opening of cyclohexane: (I) direct opening of the cyclohexane ring to give HEX, (II) isom-

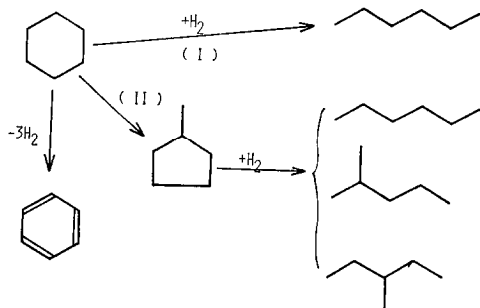


Fig. 6. A reaction scheme for ring opening of cyclohexane.

TABLE 3

Selectivity Factor in Ring Opening of Cyclohexane

Temperature (°C)	269.3	280.0	290.1	293.7	304.4
S_I	0.76	0.68	0.60	0.57	0.52

erization of cyclohexane to MCP followed by ring opening to give 2MP, 3MP, and HEX.

The selectivity for these two reaction paths is discussed as follows in terms of the relation of the selectivity factor, S_I , and the reaction temperature. S_I is defined as the ratio of the amount of HEX produced through path (I) to the sum of hexane isomers produced through paths (I) and (II). The amount of HEX produced through path (II) is estimated 20% of the amount of 2MP. Because of the fact that the composition of hexane isomers is independent of the contact time, S_I can be calculated from Eq. (1) by using the yields of hexane isomers,

$$S_I = (Y_H - 0.2Y_{2M}) / (Y_H + Y_{2M} + Y_{3M}), \quad (1)$$

where Y_H , Y_{2M} , and Y_{3M} are the yields of HEX, 2MP, and 3MP, respectively. The results calculated are given in Table 3. It is apparent that ring opening through path (I) occurs preferentially at lower temperatures, while the reaction via MCP proceeds significantly at higher temperatures.

Selectivity for Ring Opening of MCP

The values of HEX:2MP:3MP obtained by ring opening of MCP are approximately expressed as 1:5:5 over the temperature range of 230–275°C. This fact indicates that large amounts of 2MP and 3MP but a small amount of HEX are produced by this reaction. This agrees well with the results of hydrogenolysis of MCP over a

nickel powder catalyst studied by Roberti *et al.* (11). According to their data, the values of HEX:2MP:3MP obtained by the ring opening of MCP can be expressed as 1:7:10, and these values are almost constant over the same temperature range as that used in the present study.

In our previous paper, the selectivity for hydrogenolysis of C₅- and C₆-paraffins over the same nickel-alumina catalyst as that used in the present study was discussed; the predominant reaction is successive degradation to methane and a hydrocarbon containing one carbon atom less than the starting hydrocarbon, while the rupture of carbon-carbon bonds other than terminal ones to give hydrocarbons occurs only as a minor reaction, and secondary-secondary CH₂-CH₂ bonds are broken more easily than tertiary-secondary CH-CH₂ bonds in the latter reaction.

The distribution of the reaction products from MCP also suggests that the CH₂-CH₂ bond in a hydrocarbon ring can be ruptured more easily than the CH-CH₂ bond in the same ring.

Stability of the Cyclohexane Ring

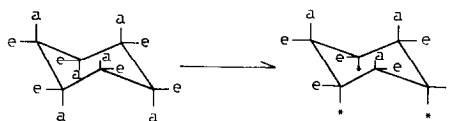
From the results obtained in this study, it is apparent that MCP is much more reactive in ring opening than cyclohexane. The reasons for the high stability of the cyclohexane ring are not completely understood yet. Bond energies of the carbon-carbon bonds in the cyclohexane ring are approximately the same as those in cyclopentane or cycloheptane ring.

Kochloeff and Bazant (3) have studied hydrogenolysis of cycloparaffins over a nickel-alumina catalyst. They have shown that methyl-groups are successively removed from their alkyl side chains without ring cleavage in the reaction of alkylcyclohexanes, while the splitting of C-C bonds in the side chains of alkylcyclopentanes and alkylcycloheptanes is accompanied by hydrogenolytic opening of the ring. They have explained the high

stability of the cyclohexane ring in terms of the formation of a surface complex of quasi-aromatic nature.

The large difference in reactivities between cyclohexane and MCP may be ascribed to the specific modes of their adsorption on the catalyst.

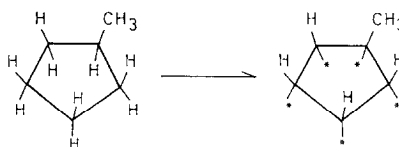
It is known that cyclohexane molecule is present practically in the chair form (A) and that the 12 hydrogen atoms may be divided into two geometrically different groups: six equatorial (e) and six axial (a) atoms.



(A) Cyclohexane molecule (B) Adsorbed model

Three hydrogen atoms in the axial position lie on one side of the ring and in the same direction. Therefore, cyclohexane seems to be adsorbed preferentially by splitting its axial hydrogen atoms on the same side of the six-membered ring parallel to the surface (B). The rupture of C-C bonds in this adsorbed species seems more difficult.

In hydrogenolysis over nickel catalysts, the C-C bond rupture proceeds via intermediates adsorbed with at least two adjacent carbon atoms such as α,β -diadsorbed species (3, 12). The formation of these species is accompanied by the deformation of bond angles in the cyclohexane ring. The stability of the cyclohexane ring may be ascribed to the strain energy and the quasi-aromatic nature of the adsorbed species.



(C) MCP molecule (D) Adsorbed model

Five hydrogen atoms in a MCP molecule are on the same side of the almost flat ring skeleton (C). It is sterically favorable for MCP to be adsorbed by splitting its hydrogen atoms on the same side without bond-angle deformation. The adsorbed species (D) may be further dehydrogenated, which may cause the ring opening.

In the present study, the formation of significant amounts of MCP from cyclohexane were observed. Isomerization of cyclohexane to MCP is usually considered to occur via a cationic mechanism. However, very little branched paraffins (below 2% of total products) were produced from hydrogenolysis of C₅-C₈ *n*-paraffins (9), and CH₂-CH₂ bonds are broken more easily than CH-CH₂ bonds in the reaction of branched paraffins and MCP over the same catalyst as the present one in the temperature range of 230-330°C. In addition, the alumina used as the support did not present any significant activity against isomerization such as cyclohexene to methylcyclopentene. From these results it is suggested that isomerization of cyclohexane to MCP proceeds via another mechanism than a cationic mechanism. It can be explained by assuming recyclization of the ring-opening intermediates. As described above, extensively dehydrogenated species lead to the C-C bond rupture. The intermediates formed by ring opening are still bound to the catalyst surface and may be either desorbed to give *n*-hexane or

recyclized to give MCP. Two alternative paths for ring opening of cyclohexane are ascribed to the behavior of the acyclic adsorbed species. At higher temperatures, the acyclic adsorbed species change into surface intermediates with extensively dissociated carbon-hydrogen bonds and the recyclization to MCP occurs in preference to the direct opening of the ring.

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