AN INVESTIGATION ON
POSSIBLE ISOMERS OF CYCLOHEXANE

by

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Introduction.

Some evidence of the existence of two isomers of cyclohexane could be taken from the variation in freezing points and other properties of samples prepared by different methods. At the same time these variations may be due entirely to differing amounts of impurities such as methyl cyclopentane, since there is some evidence in the literature that this may be formed in the catalytic hydrogenation of benzene.¹

One form may be produced by the reduction of benzene in the gaseous state using nickel as a catalyst and the other by the hydrogenation of benzene in the liquid state with platinum black as a catalyst.

The tetrahedral structure of carbon atom bonds allows two possible steric-isomeric forms of cyclohexane.²³⁴ Photographs of models of these possible isomers are shown. It will be noticed that model I. is the more symmetrical and the arrangement of the bonds hold the atoms rigidly in that structure. In model II. the carbon atoms may rotate about the bonds within definite limits but the same relative positions of the carbon atoms are always maintained.

Experimental.

Benzene was hydrogenated by the method of Sabatier and Senderens as given in Marted’s "Catalytic Hydrogenation".⁵
In preparing the catalyst a solution of nickel nitrate and magnesium nitrate was treated with sodium hydroxide. The precipitate was filtered, thoroughly washed with distilled water, then spread in a layer about one quarter of an inch thick on a clean nickel sheet. The material was cut into briquettes while being gradually dried by a moving bunsen flame under the sheet. The briquettes were reduced in a current of hydrogen at 300°C.

Hydrogen was produced in a Kipp generator and bubbled through alkaline permanganate solution, sodium pyrogallol solution and concentrated sulphuric acid before entering the tube containing the catalyst. Thiophene free benzene was dropped from a burette into the tube at the hydrogen inlet.

The outlet of the hydrogenation apparatus was connected to a condenser, and an air tight receiver with a side tube that allowed the excess hydrogen to bubble out through water. This prevented the entrance of oxygen to the apparatus.

According to Maxted the optimum temperature for this reduction is about 250°C. At this temperature benzene was passed through a 2.5 cm. pyrex tube one metre long filled with the reduced briquettes. After passing the sample through the apparatus fifty times at the rate of about fifty cubic centimetres of liquid in three hours the composition of the product remained constant at 12% cyclohexane. This value was determined from a curve of refractive index vs. composition of benzene-cyclohexane mixtures obtained from data given by Burrows and Lucarini.
No difference was found after treating the catalyst with hydrogen only, at 300°C for several days. Then an apparatus was built containing five tubes of catalyst, the same size as the first, placed side by side and connected in series. After the catalyst was reduced as before the product from the first apparatus was passed through this one heated to 250°C. The composition of the sample remained constant at 18% cyclohexane, determined as before, after twenty five passes through the apparatus.

It was found that the optimum temperature most generally recommended in the journals for this reduction was between 160 and 180°C. After passing through the apparatus ten times, at 170°C, the refractive index of the sample was lower than that of cyclohexane. There was no change in the refractive index after the sample was treated with concentrated sulphuric acid, washed with sodium hydroxide and distilled over sodium. The freezing point of the product was found to be -40°C.

An attempt was made to reduce benzene to cyclohexane in the liquid state with a suspension of finely divided platinum. The method used was that of Lowe as described by Willstatter and Hartt. Platinum scraps were dissolved in aqua regia, the solution was diluted, neutralized with sodium hydroxide and a solution of formaldehyde was added until no further precipitation resulted. The reduced platinum was allowed to settle in a tall cylinder and the solution was decanted off. The platinum was washed by decantation until the wash water showed
no test for chlorine. By this means six grams of floculent platinum black was obtained. This was placed in a flask with 55.5 grams of thiophene free from benzene and 75 c.c. of glacial acetic acid. The flask was clamped on a reciprocating shaker and hydrogen was lead into it through a tube in a tight stopper. The hydrogen was stored in a gas holder and lead through a purification train before entering the flask. The flask and purification train were evacuated before admitting hydrogen.

Hydrogen was absorbed rapidly at the start of the reduction, but at the end of two hours the rate of absorption was very slow, and the decrease in volume of hydrogen in the gas holder was only about 15% of the amount theoretically required for the reduction. The operation was continued for several days. The apparatus was evacuated periodically to remove any possible accumulation of inert gases. The resulting hydrocarbons were separated from the catalyst and acetic acid by adding water and decanting. The product was thoroughly washed with water then dried over sodium. It was treated with liquid sulphur dioxide at -13°C and was found to be completely miscible. The platinum was redissolved and reprecipitated and the operation was repeated with practically the same results. The catalyst in this reduction seems to be very easily poisoned. The glacial acetic acid may have contained some impurities although it was purified by recrystallization several times.

Two commercial samples of cyclohexane, represented as
being chemically pure, were treated in an attempt to obtain isomers. One sample was from the Eastman Kodak Company and the other from the British Drug House. These samples were refluxed with concentrated sulphuric acid, washed with sodium hydroxide, dried with calcium chloride and distilled over sodium. They were carefully fractionated by the use of a column 90 cm. long, filled with glass beads and connected to a reflux condenser at the top. The temperature of the condensing reflux increased slowly and uniformly throughout the entire distillation. Each sample was divided into four fractions. The freezing point of each was determined in a freezing point apparatus having an air space between the freezing vessel and cooling bath. Temperatures in the cyclohexane were read with a Beckman thermometer. No sharp freezing point was found for any of the fractions. Temperatures were read at intervals of time and the temperature at which the cooling curve changed its slope was taken as the freezing point. The refractive indexes were determined with a Bausch and Lomb dipping refractometer. Densities were determined with a picnometer.
A previous worker, Mr. Selwood\(^8\), claims to have obtained pure cyclohexane which had a freezing point of 4.28°C varying not more than 0.02°C during the entire solidification. His method of purification was as follows: He refluxed about 300 c.c. of cyclohexane from Eastman Kodak Company over sodium for eight hours and slowly distilled. He then placed the cyclohexane in an ice bath and stirred it vigorously until it froze in a white cloud. He decanted the liquid through a filter of glass wool and collected the cyclohexane remaining on the filter separately and repeated the freezing process with the unfrozen liquid until only about 10% of the original liquid remained. He discarded this portion and repeated the process eleven times in air and twice in vacuum. He gives the refractive index of the product as 1.4266. His results were partly responsible for
the present investigation. It will be noticed that the only freezing point in the table given above, as low as that obtained by this man, is that for the lowest boiling fraction and its other physical constants do not agree with those for cyclohexane.

An attempt was made to separate two isomers from cyclohexane by fractional crystallization. For this purpose a mechanical refrigerator was built with a vertical helical expansion coil enclosed in a heat insulated box. The coil was about two inches larger in diameter than a winchester. The bottom was cut out of a winchester and it was inverted in the cooling chamber. A wire screen and glass wool filter were placed in the neck and a tube lead from it through the bottom of the insulated box to the stop cock. About one and a half litres of cyclohexane were placed in the winchester. The cyclohexane was stirred with a bent glass rod connected through the top of the box to an electric stirring motor. The temperature of the air in the cooling box was gradually reduced until flakes of cyclohexane were observed through a window in the box. The temperature was then kept within a range of 0.2°C by the use of toluene thermostat in the box operating on a relay connected to the compressor motor. The crystals, kept in suspension by stirring, were maintained at equilibrium with the liquid for several hours. Then the drain cock was opened and the liquid was drawn out of the chamber leaving the crystals behind on the filter. This process was repeated several times
on both fractions but no indication of two fractions with a constant freezing point were obtained.

Discussion.

A comparison of the physical properties of cyclohexane from various sources is given below. The first two sets of values in the table are those obtained in this research for the most pure fraction of cyclohexane from the Eastman Kodak Company and the British Drug House, respectively. The third is for the product obtained by the hydrogenation of benzene as described. For the others, the numbers in the left hand column refer to the bibliography.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Boiling Point</th>
<th>Freezing Point</th>
<th>Refractive Index</th>
<th>Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>79.5</td>
<td>6.37</td>
<td>1.42380</td>
<td>.7768</td>
</tr>
<tr>
<td></td>
<td>80.4</td>
<td>6.077</td>
<td>1.42377</td>
<td>.7782</td>
</tr>
<tr>
<td></td>
<td>-40.</td>
<td>1.42348</td>
<td>.7755</td>
<td></td>
</tr>
<tr>
<td>9.Pt.catalyst</td>
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<td>1.42476</td>
<td>.7783</td>
<td></td>
</tr>
<tr>
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<td>1.42496</td>
<td>.7782</td>
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<tr>
<td>10</td>
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<td></td>
</tr>
<tr>
<td>11</td>
<td>80.75</td>
<td>6.63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>80.1</td>
<td>1.4266</td>
<td>.7786</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>81.4</td>
<td>6.5</td>
<td>1.4273</td>
<td>.779</td>
</tr>
<tr>
<td></td>
<td>4.28</td>
<td>1.4266</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl cyclopentane</td>
<td>73</td>
<td>-140.5</td>
<td>1.40750</td>
<td>.750</td>
</tr>
</tbody>
</table>
By comparing the physical constants of the product obtained by the catalytic hydrogenation of benzene as described, with those of methyl cyclopentane, it is quite evident that a considerable amount of the latter contaminated the product. It seems reasonable to conclude that at least a small fraction of the benzene, under other conditions of reduction, undergoes an interatomic change to give methyl cyclopentane instead of cyclohexane.

Nagornor and Ratinjanz\textsuperscript{11} give the latent heat of fusion of cyclohexane as 7.73 calories per gram at 6.7°C. Substituting these values in the modified Clansius-Clapeyron equation

\[
\Delta T = \frac{RT^2}{\Delta H_T} x
\]

we get the mol fraction of impurity for a one degree change in freezing point given by

\[
1 = \frac{1.99(279.7)^2}{7.73(84)} x
\]

\[
x = .00418
\]

If we consider the impurity to be methyl cyclopentane this gives .418% impurity. The above equation is only approximately true but it gives a result of the order that would account for the variation in observed freezing points.

Muhammad Qudrat-I-Khada\textsuperscript{4} bases his investigation partly on isomers of substitution products of cyclohexane. Since all of the hydrogen atoms, in one of the possible forms, are not equivalent it is possible to obtain isomers of substitution products without the necessity of isomers of the hydrocarbon.
In conclusion it seems that there is not enough evidence for the existence of two distinct isomers of cyclohexane. At the same time, the presence of methyl cyclopentane does not prove the absence of the two forms. There may be an equilibrium between the two possible forms or one may be more stable than the other. Finally the existence of strainless forms is only a hypothesis which may not be true owing to unknown forces between the atoms.
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