

[CONTRIBUTION FROM THE RESEARCH LABORATORIES DIVISION OF THE GENERAL MOTORS CORP.]

The Isomerization of Cyclohexane and Methylcyclopentane¹

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Recently Montgomery, McAteer, and Franke² reported a reversible isomerization of the butanes occurring in the presence of aluminum bromide. Since the isomerization was unaccompanied by side reactions, it offered a method for experimentally determining the equilibrium constant.

In view of Montgomery's success, we decided to study the reversible isomerization of cyclohexane and methylcyclopentane reported by Nenitzescu and Cantuniari.³ These investigators found cyclohexane or methylcyclopentane to rearrange in the presence of moisture-containing aluminum chloride to give an equilibrium mixture containing approximately 22% methyl cyclopentane. In addition, a small amount of saturated hydrocarbon, suspected to be *n*-hexane, was produced. Other investigators have not found the reaction products of aluminum chloride and cyclohexane to be as simple as reported by Nenitzescu. In addition to methylcyclopentane, Zelinsky⁴ also reports dimethylcyclobutane as one of the reaction products. Ipatieff and Komarewsky⁵ also found methylcyclopentane among the reaction products of cyclohexane and aluminum chloride, but 34% of the reaction products boiled higher than cyclohexane and consisted of 34% dimethylcyclohexane and 66% of a mixture containing dicyclohexyl and dimethyldicyclopentyl. These experiments, however, were carried out in closed autoclaves at 150°, and represent quite severe conditions.

In general, our results at lower temperatures confirm the findings of Nenitzescu. The anhydrous aluminum chloride was inert toward the hydrocarbons and the addition of water or hydrogen chloride was required to effect reaction. The reactions were remarkably clean, and the gas and tar which usually characterize the action of aluminum chloride on hydrocarbons were completely absent, even in experiments lasting as

(1) Presented before the Symposium on the Role of Catalysis in Petroleum Chemistry held by the Petroleum Division at the Baltimore meeting of the American Chemical Society, April 3-7, 1939.

(2) Montgomery, McAteer and Franke, *THIS JOURNAL*, **59**, 1768 (1937).

(3) Nenitzescu and Cantuniari, *Ber.*, **66**, 1097 (1933); see, also, *Aschan, Ann.*, **324**, 1 (1902); Grignard and Stratford, *Compt. rend.*, **178**, 2149 (1924).

(4) Zelinsky and Turowa-Pollak, *Ber.*, **65**, 1171 (1932).

(5) Ipatieff and Komarewsky, *THIS JOURNAL*, **56**, 1926 (1934).

long as seven weeks. Also, the aluminum chloride remained clean and powdery and only a slight discoloration occurred. However, when aluminum bromide was substituted for aluminum chloride, a tarry lower layer was formed and isobutane was evolved.

Distillation of relatively large amounts of the reaction products in an 80-plate column showed them to consist almost exclusively of a mixture of cyclohexane and methylcyclopentane; refractive index measurements of the initial distillate and distillation residue indicated only traces of other products to be present. Fractionation of 15 liters of cyclohexane-aluminum chloride reaction product indicated that not more than about 5% of the cyclohexane reacting is consumed in side reactions which accompany the isomerization. Branched chain hexanes, methylcyclohexane, 1,3-dimethylcyclohexane, dicyclohexyl, and dimethyldicyclopentyl are the probable products of the side reactions.

Since isomerization appeared to be practically the sole reaction, experimental determination of the equilibrium constant and the effect of temperature on it were next studied. Experiments were carried over the temperature range 25 to 77.4° (boiling temperature) at 10° intervals, in which the equilibrium was approached from both sides. The course of the reaction was followed by the change in the refractive index. The data obtained are shown in Table I and Fig. 1.

TABLE I
EQUILIBRIUM CONCENTRATIONS OF METHYLCYCLOPENTANE

Reaction temp., °C.	Approach to equilibrium from cyclohexane side		Approach to equilibrium from methylcyclopentane side		Average mole % methylcyclopentane
	<i>n</i> _D ²⁰	Mole % methylcyclopentane	<i>n</i> _D ²⁰	Mole % methylcyclopentane	
25	1.4242	11.70	1.4239	13.30	12.5
35	1.4238	13.95	1.4236	15.00	14.5
45	1.4234	16.15	1.4234	16.15	16.2
55	1.4229	18.95	1.4228	19.50	19.2
65	1.4225	21.10	1.4224	21.70	21.4
77.4	1.4217	25.60	1.4217	25.60	25.6

Assuming the cyclohexane-methylcyclopentane solutions to be ideal, the data of Table I were used to calculate the equilibrium constant and ΔF° , by means of the equation $\Delta F^\circ = -RT \ln K$ for the

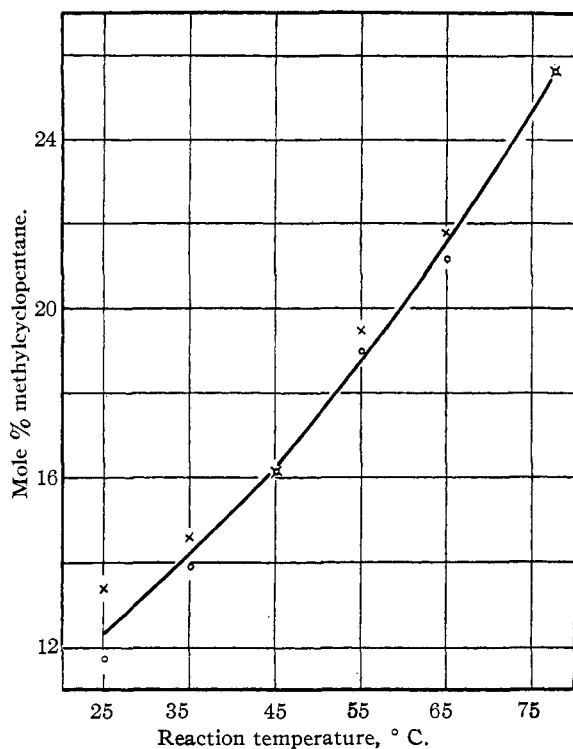


Fig. 1.—Composition of cyclohexane-methylcyclopentane equilibrium mixtures. X, Equilibrium approached from methylcyclopentane side; O, Equilibrium approached from cyclohexane side.

liquid phase reaction: cyclohexane \rightarrow methylcyclopentane. These results are shown in Table II.

TABLE II
EQUILIBRIUM BETWEEN CYCLOHEXANE AND METHYL-
CYCLOPENTANE

Reaction temp., °C.	K	ΔF°
25	0.143	1150
35	.170	1085
45	.193	1040
55	.238	936
65	.272	875
77.4	.344	743

The values of ΔF° and K were used to calculate the heat of reaction and the entropy change. The heat of reaction was calculated by the use of the van't Hoff equation, $d(-R \ln K)/d(1/T) = \Delta H$, and the entropy change calculated from the equation $\Delta F = \Delta H - T\Delta S$. The thermodynamic constants obtained from the equilibrium measurements are summarized in Table III and compared with the results of Parks.⁶

(6) Parks and Huffman, "The Free Energies of Some Organic Compounds," A. C. S. Monograph Series No. 60, The Chemical Catalog Co., New York, 1932; Huffman, Parks and Barmore, *THIS JOURNAL*, **53**, 3876 (1931); Parks, Huffman, and Thomas, *ibid.*, **52**, 1032 (1930); Parks, paper presented at the Washington meeting of the Am. Chem. Soc., 1933.

TABLE III
THERMODYNAMIC CONSTANTS FOR THE REACTION: CYCLO-
HEXANE (liq., 25°) \rightarrow METHYL-CYCLOPENTANE (liq., 25°)

	Calcd. from equilibrium measurements	Calcd. from third law by Parks
ΔH , cal.	3510	-1100
ΔS , e. u.	7.9	10
ΔF° , cal.	1150	-4100

With the exception of ΔS , the constants obtained by the different methods are in rather poor agreement. Parks' value for ΔH is based on earlier work⁷ on the heats of combustion of the two hydrocarbons. The combustion data, particularly that of methylcyclopentane, are rather uncertain and considering the magnitudes of the heats of combustion, it is probable that their small difference, or ΔH , contains considerable error. With Parks' method of calculation any error in ΔH is, of course, carried over to ΔF° .

Experimental

Materials and Analytical Methods.—The cyclohexane used in the experiments for the identification of the reaction products was a c. p. grade manufactured by the Eastman Kodak Company. Distillation of this material indicated a negligible quantity of higher-boiling impurity. The cyclohexane used for the study of the equilibrium constants was a constant boiling fraction distilled from the Eastman Kodak Company material and had a refractive index of 1.4262 at 20°. The methylcyclopentane was prepared by the action of aluminum chloride on cyclohexane. Only the constant boiling fraction having a refractive index of 1.4100 at 20° was used. Baker c. p. anhydrous aluminum chloride was used throughout without further purification. The aluminum bromide was prepared by the action of bromine on aluminum.

Unless otherwise stated, the fractionating column used throughout this work was a spiral-packed, vacuum-jacketed, automatic recording and controlled column having 80 theoretical plates and a low holdup (40 cc.).

A series of methylcyclopentane-cyclohexane mixtures were prepared and the refractive indices determined with an Abbe-Zeiss refractometer, with temperature control within 0.2° by an independent cooling and circulating system. A plot of the data given in Table IV was used to obtain refractive index analyses.

TABLE IV
REFRACTIVE INDICES OF METHYL-CYCLOPENTANE-CYCLO-
HEXANE MIXTURES

Mole % methyl- cyclopentane	7.19	13.26	19.89	24.91	29.95	35.01
n_D^{20}	1.4250	1.4238	1.4227	1.4219	1.4210	1.4200

The Action of Aluminum Chloride on Methylcyclopentane.—For a quantitative experiment, 750 cc. of methylcyclopentane, 150 g. of anhydrous aluminum chloride, and 5 cc. of water were placed in a 2-liter flask equipped with a reflux condenser connected to a gas receiver. The

(7) Kharasch, *Bur. Sids. J. Research*, **2**, 374 (1929).

reaction mixture was boiled for three hours, the reaction flask was then cooled, the liquid decanted, and washed with water. Tar and gas were not formed in this experiment. After drying, 650 cc. of product remained, indicating a loss of 100 cc. Absorption of the liquid by the aluminum chloride and the drying agent probably accounts for the principal part of the loss, washing and handling account for the remainder. The dried product had a refractive index of 1.4220 at 20°, which, according to the data of Table IV, indicates the presence of 24.0 mole % methylcyclopentane.

For the distillation analysis, 600 cc. of the product was used. The distillation curve obtained is shown in Fig. 2. Altogether 536.8 cc. was distilled, leaving a residue of 58 cc. with a refractive index of 1.4282 at 20°, indicating that part of the residue consisted of material boiling higher than cyclohexane. The first 11 cc. of distillate also had a refractive index 0.0022 lower than pure methylcyclopentane. However, the products of the side reactions are relatively small in quantity and the mixture can be considered as consisting solely of methylcyclopentane and cyclohexane. The distillation curve shows 151.5 cc. methylcyclopentane and 448.5 cc. cyclohexane. Converting to mole % gives 24.6 mole % methylcyclopentane, a figure which compares favorably with the 24.0 mole % found by refractive index measurements.

The Action of Aluminum Chloride on Cyclohexane.—Preliminary experiments indicated similarity between the cyclohexane-aluminum chloride and methylcyclopentane-aluminum chloride reactions. The addition of water to the anhydrous aluminum chloride was found to be necessary to promote reaction and the reaction products were free of tar and gas.

A quantitative experiment was made to discover the reaction products and to test the feasibility of using refractive index measurements as a method of analysis: 1500 cc. of cyclohexane, 300 g. of aluminum chloride, and 6.5 cc. of water were boiled for three hours in the same apparatus as used in the methylcyclopentane experiment. The reaction product was then cooled, the clear liquid decanted, washed, and dried; 1270 cc. of dried material was recovered having a refractive index of 1.4225 at 20°. The data of Table IV show this to be equivalent to 21.0 mole % methylcyclopentane. Distillation of 1200 cc. of this material gave a curve similar to that shown in Fig. 2, and showed the mixture to contain 250 cc. of methylcyclopentane and 950 cc. of cyclohexane. These volumes correspond to 20.2 mole % methylcyclopentane which compares favorably with the 21.0 mole % found by refractive index measurements. In this distillation, the first 30 cc. of distillate had a refractive index of 1.4087 at 20° and the 508 cc. of residue had a refractive index of 1.4266 at 20°, indicating that side reactions had occurred to a slight extent.

The products and extent of the side reactions were determined in a similar type of experiment in which a total of approximately 15 l. of cyclohexane was treated with aluminum chloride. Distillation in an 80-plate column gave 2.5

l. of pure methylcyclopentane, 50 cc. of material boiling below methylcyclopentane, and 97 cc. of material boiling above cyclohexane. Redistillation of the lower boiling material in a 28-plate column and refractive index measurements suggested the presence of only paraffinic constituents. The bulk of the material distilled in one plateau at 61°. The n_D^{20} of this material was 1.3756, and it was probably a mixture of isomeric hexanes; however, the small amount did not allow complete separation. No trace of *n*-hexane could be detected. Redistillation of the higher boiling material revealed three plateaus: 20 cc. boiled at 99.5°, 25 cc. at 119.5°, and 30 cc. from 208 to 220°. The 99.5° material is probably methylcyclohexane, although

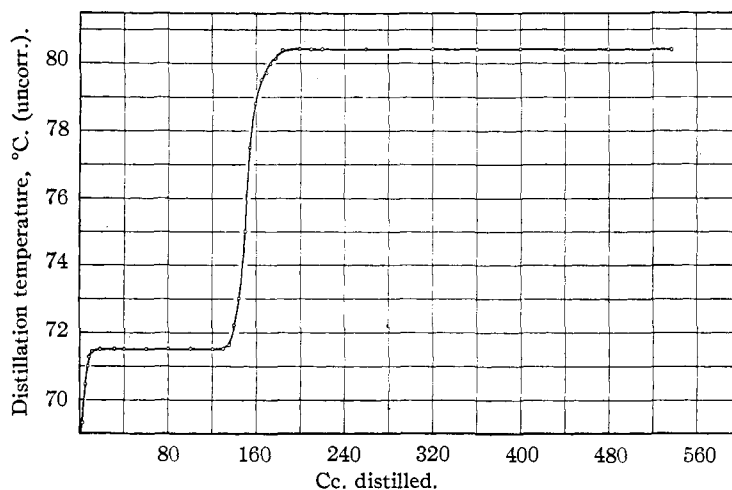


Fig. 2.—Distillation of 600 cc. methylcyclopentane-aluminum chloride reaction mixture. Distillation residue, 58 cc.

the refractive index of 1.4212 at 20° is somewhat low. The 119.5° material had a refractive index of 1.4237 and is probably 1,3-dimethylcyclohexane, since a product with these constants has been identified as such by Ipatieff.⁵ The material boiling from 208 to 220° and having a refractive index of 1.4680 to 1.4703 undoubtedly consists of dimethyldicyclopentyl and dicyclohexyl, as reported by Ipatieff⁶ and Nenitzescu.⁸ On the basis of this experiment, not more than about 5% of the cyclohexane reacting is consumed in side reactions which accompany the isomerization.

The Action of Aluminum Bromide on Cyclohexane.—Previous work⁹ with paraffins suggested that aluminum bromide could be substituted advantageously for the chloride. However, when the bromide was used with cyclohexane, tar formation and gas evolution resulted. Also, appreciable quantities of paraffins boiling lower than methylcyclopentane were formed. Isobutane, isopentane, and the isomeric hexanes were among the reaction products.

The Cyclohexane-Methylcyclopentane Equilibrium.—The apparatus used in these experiments consisted of a 200-cc. reaction flask fitted with a reflux condenser. The top of the condenser connected to a drying tube, the other end of which was open to the atmosphere. The reaction

(8) Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931).

(9) Glasebrook, Phillips and Lovell, *THIS JOURNAL*, **58**, 1944 (1936).

flasks were immersed in a constant temperature bath which maintained the temperature within 0.5°.

Although experiments had shown the equilibrium to be independent of catalyst concentration, nevertheless, uniform quantities, consisting of 100 cc. of hydrocarbon, 30 g. of aluminum chloride, and 1 cc. of water, were used in each experiment. At each temperature studied, simultaneous experiments were made to approach the equilibrium from both sides.

In the preliminary experiments it was also noted that the reaction undergoes an induction period. If the aluminum chloride, water, and hydrocarbon are mixed and allowed to stand at room temperature, refractive index measurements indicate very little reaction, even after several days of standing. If, however, the reaction mixture was heated to boiling, reaction started within fifteen minutes. In view of this fact, the reaction flasks were always boiled for a few minutes after the reactants were mixed to initiate the reaction. Samples were withdrawn at the end of the boiling period, and refractive index measurements made to make certain that the reaction mixtures were still far removed from the probable equilibrium. The reaction flasks then were placed in the constant temperature bath. Periodically, samples of the reaction mixture were withdrawn by inserting a glass tube down through the reflux condenser. The samples immediately were washed, dried, and analyzed by means of refractive index measurements. The reac-

tions were continued until the refractive indices reached and maintained a constant value. Constant values were reached in about two hours at the boiling point, but three or four weeks were required at the lower temperatures.

The data obtained are presented in Table I.

Summary

1. The reaction of cyclohexane or methylcyclopentane in the presence of anhydrous aluminum chloride promoted by water results in an equilibrium mixture consisting principally of the two hydrocarbons. In the case of cyclohexane, the side reactions amount to approximately 5% based on the quantity of cyclohexane isomerized.

2. The equilibrium constants for the isomerization reaction have been determined at 10° intervals from 25° to the boiling temperature (77.4°).

3. From these data, values of the free energy change, heat of reaction, and entropy change for the isomerization reaction have been computed and compared with values calculated from heat capacity data.

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[CONTRIBUTION FROM THE KENT AND GEORGE HERBERT JONES LABORATORIES, UNIVERSITY OF CHICAGO]

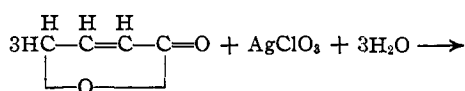
The Reduction of *dl*-Erythronic Lactone to *dl*-Erythrose¹

BY J. W. E. GLATTFELD AND B. D. KRIBBEN

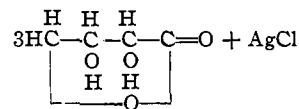
For some years past, work on the preparation and study of the eleven C₄-saccharinic acids has been carried on in these Laboratories.² The work, which is now completed, was done in order to provide data on the constants and properties of these acids that might be useful in detecting them in, and separating them from, reaction mixtures produced by the action of alkalis on the tetroses.

The next step in the program is the synthesis of the *dl*-tetroses themselves. A source of one of these tetroses, *dl*-erythrose, has been found in *dl*-erythronic lactone which is prepared by the oxidation of the lactone of γ -hydroxy-isocrotonic acid, obtained as a by-product in the synthesis of one of the C₄-saccharinic acids.³ The oxidation

is achieved with osmium tetroxide-activated silver chlorate⁴ according to the equation



Lactone of γ -hydroxy-
isocrotonic acid



dl-Erythronic lactone

Some success has been attained in the conversion of the *dl*-erythronic lactone so obtained into *dl*-erythrose. This paper gives an account of the work.

The optically active forms of the aldotetroses seem to be fairly well known, the constants of the tetroses⁵ resting, perhaps, on a somewhat firmer

(1) This article is condensed from a dissertation presented by B. D. Kribben in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Chicago.

(2) Glattfeld and co-workers, *THIS JOURNAL*, **42**, 2314 (1920); **43**, 2675 (1921); **47**, 1742 (1925); **49**, 2309 (1927); **53**, 3164 (1931); **55**, 1114 (1933); **55**, 3663 (1933); **60**, 415 (1938).

(3) Glattfeld, Leavell, Spieth and Hutton, *ibid.*, **53**, 3164 (1931).

(4) (a) Hilmeyer Cohen, Ph.D. dissertation, University of Chicago, 1928; (b) Géza Braun, *THIS JOURNAL*, **51**, 235 (1929).

(5) Hockett, Deulofeu, Sedoff and Mendive, *ibid.*, **60**, 278 (1938).