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The Isomerization of Cyclohexane and Methylcyclopentane in the Presence of Aluminum Halides. II. Equilibrium and Side Reactions

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Introduction

In the preceding paper with the same title, there were presented the results of a set of experiments designed to elucidate the nature of the catalysis of the interconversion of cyclohexane and methylcyclopentane. In the course of this work considerable data were acquired on the equilibrium constant of the isomerization reaction, as well as on the nature and relative rates of the side reactions which accompany the isomerization reaction. The equilibrium between cyclohexane and methylcyclopentane has been the subject of several previous investigations.[1] The results of the previous investigators are concordant with and confirmed by the present work. Despite the apparent duplication, it seems worth while to record our results in view of the very different and probably more reliable analytical methods at our disposal. In the equilibrium studies particular attention was devoted to the possible presence of the various cyclobutanes and cyclopropanes, isomeric with cyclohexane and methylcyclopentane, which have been reported to be formed by the action of moist aluminum bromide on cyclohexane.[2]

Paraffins, C_7 and C_8 naphthenes, and bicyclanes have been identified among the products of the side reactions accompanying the interconversion of cyclohexane and methylcyclopentane catalyzed by aluminum halides. It was of particular interest to determine whether or not cyclopentane accompanies the formation of the higher naphthenes as might be expected by analogy with formation of isobutane and hexanes in side reactions accompanying the interconversion of iso- and normal pentane.

Experimental

The experiments were carried out by the methods described in the preceding paper, using the materials therein described, with the exceptions noted below.

Purified aluminum bromide, ground to a fine powder in a dry box (dried by spreading Dry Ice on the bottom), was used after exposure to atmospheric moisture to assure catalytic activity. Cyclopentane was prepared by hydrogenation of carefully purified cyclopentadiene. The crude cyclopentane was fractionated in a high efficiency column and residual traces of cyclopentadiene and cyclopentene were removed by percolation through activated silica gel (Davco, 28–200 mesh) and shaking with a small portion of moist aluminum chloride. After the aluminum chloride treatment, the cyclopentane was subjected to a trap (room temperature) to trap (liquid nitrogen) vacuum distillation. The mass and infrared spectra of the final cyclopentane showed the presence of no detectable impurity.

In a number of the experiments the reaction product was separated from the catalyst by a high vacuum distillation. The reaction tube was opened with the contents chilled with liquid oxygen and connected to the vacuum system by means of a short length of rubber tubing. After evacuation, the pump was cut off from the manifold, and the liquid oxygen was transferred to a weighed trap affixed to the manifold by means of a standard taper joint. The reaction tube was permitted to warm slowly to room temperature. The distillation was stopped approximately five minutes after the reaction tube attained room temperature. The product so collected is defined as the volatile product.

The traps were constructed with a stopcock so that the samples could be stored while awaiting analysis without danger of loss of volatile components. The stopcocks were of the pressure type and were lubricated with a hydrocarbon insoluble grease compounded of mannitol, starch and anhydrous glycerol. A section of tubing packed with ascarite was interposed between the reaction tube and collecting trap to remove hydrogen halide and entrained catalyst.

The products of all experiments were examined with the mass spectrometer in order to determine the extent of the side reactions and the applicability of the infrared spectrophotometric method for determining methyl cyclopentane and cyclohexane. The products of the experiments in which the side reaction was excessive were subjected to analytical distillation to give three fractions, (1) boiling below 65°, (2) boiling from 65 to 85°, and (3) boiling above 85°. These fractions were analyzed with the mass spectrometer.

The results of the experiments on the cyclohexane–methylcyclopentane reaction at 27, 59 and 100°, are summarized in Tables I, II, and IIIa, and IIIb, respectively. The experiments with cyclopentane at 100° are described in Table IV.

In all the experiments on the reaction of the C_6 naphthenes with aluminum bromide the reacting system remained a clear, colorless solution. In the 60° experiments, the aluminum chloride retained its white, granular appearance. The aluminum chloride–C_6 naphthene system at 100° rapidly changed from a liquid–solid system to one of two liquid phases. The more dense phase acquired a very faint yellow color. Upon cooling to room temperature the more dense phase became very viscous, and white crystals precipitated from it very slowly. When the 100° reaction tubes were opened, the unfrozen film of the denser phase at the top of the tube became bright red very quickly and then slowly darkened until it became black. The non-volatile residues from the vacuum separation of the product of the 100° experiments were hydrolyzed in the cold (0°) with 6 *N* sodium hydroxide solution. From the resultant mixture a dark yellow to brown, viscous oil was recovered. The depth of color increased with time. This oil as first recovered was soluble in isoöctane, but from the isooctane solutions a brown, resinous substance slowly precipitated on standing in contact with air. It was found that a colorless oil could be recovered from the deeply colored oil by means of a high vacuum (10^{-4} mm.) distillation from a trap at room temperature to one at liquid nitrogen temperature.

The formation of two liquid phases from the solid–liquid system aluminum chloride–aromatic has been often described. However, the more dense phase formed when paraffins, olefins, or aromatics are the hydrocarbon components of the system is very deeply colored (orange to

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[1] (a) Glasebrook and Lovell. THIS JOURNAL, 61, 1717 (1939); (b) Schmidt, Hoog and Verheus. *Rec. trav. chim.*, 59, 793 (1940); (c) Mizusima, Morino and Fujisiro, *J. Chem. Soc. Japan*, 62, 587 (1941).

[2] Zelinsky and Turowa-Pollak, *Ber.*, 65, 1171 (1932).

TABLE I

REACTION OF CYCLOHEXANE AND METHYLCYCLOPENTANE IN THE PRESENCE OF MOIST ALUMINUM BROMIDE AT 27.0 ± 0.5°

Expt. no.	Iden.	C_6H_{12} m. × 10^3	Al_2Br_6 m. × 10^3	Time, hr.	MCP/CH		Mole %[a]					
					M. S.[a]	I. R.[b]	C_5H_{10}[c]	C_5H_{12}	C_6H_{14}[d]	C_7H_{14}[c]	C_8H_{16}[c]	$C_{12}H_{22}$[e]
1[h]	CH	46	1.38	24	[f]	0.048[g]	....	....	...	....	....	....
2[h]	MCP	44	1.25	24	...	.230[g]	....	....	...	....	....	....
3[h]	MCP	44	1.21	256	0.132	.112	<0.05	<0.03	0.4	0.05	0.05	0.2
4[h]	CH	46	1.16	256	.135	...	< .05	< .03	< .1	< .01	< .01	< .02
5[h]	MCP	44	0.94	313	.147	.150	< .05	< .03	.5	...	....	....
6[h]	CH	46	0.95	313	.109	...	< .05	< .03	< .1	< .01	< .01	< .01
7[h]	MCP	44	1.07	352	...	.113	....	....	...	....	....	....
8[h]	CH	46	0.88	352	.142	...	< .05	< .03	< .1	< .01	< .01	< .01
9[i]	CH	46	0.82	352	.136	.121	< .05	< .03	< .1	....	....	....
10[i]	MCP	44	0.85	352	.135	.146	< .05	< .03	< .1	....	....	....
				Average	0.134	0.129						
					±0.008	±0.016						
					0.132	±0.012						

[a] Mass spectrometric analysis. [b] Infrared analysis. [c] Calculated as naphthene. [d] Calculated as methylpentane. [e] Calculated as dicyclohexyl. [f] Dots (...) indicate not determined. [g] Omitted from average. [h] Products recovered by hydrolysis. [i] Product recovered by distillation. Analysis reported, that of all material boiling below 85°. Over 99.7%w of the hydrocarbon was recovered by the vacuum distillation and less than 1% of the recovered hydrocarbon boiled above 85°.

TABLE II

THE REACTION OF CYCLOHEXENE AND METHYLCYCLOPENTANE IN THE PRESENCE OF MOIST ALUMINUM CHLORIDE OR BROMIDE AT 59.0 ± 0.5°

Expt. no.	Iden.	C_6H_{12} m. × 10^3	Al_2Cl_6 m. × 10^3	Time, hr.	MCP/CH		Mole %					
					M. S.[a]	I. R.[b]	C_5H_{10}[c]	C_5H_{12}	C_6H_{14}[d]	C_7H_{14}[c]	C_8H_{16}[c]	$C_{12}H_{22}$[e]
11[h]	CH	46	2.5	256	0.255	0.246	<0.05	<0.04	0.2	0.04	0.04	0.65
12[h]	MCP	44	3.5	256	.252	.241	< .05	< .04	.3	0.05	.05	.71
13[h]	CH	46	2.4	282	.238	.232	< .05	< .04	.2	.03	[f]	...
14[h]	MCP	44	3.1	282	.230	.228	< .05	< .04	.2	.04	.06	.66
15[i]	MCP	44	2.7	330	.246	.249	< .05	< .04	.2	....	....	...
16[h]	CH	46	0.36[j]	119	.256	...	< .05	< .05	< .1	< .04	< .04	...
17[h]	CH	46	2.0	96	.230	...	< .05	< .05	< .1	< .04	< .04	...
				Average	0.244	0.239						
					±0.010	±0.080						

[a] through see notes to Table I. [j] Aluminum bromide was used in this experiment.

TABLE IIIa

REACTION OF CYCLOHEXANE AND METHYLCYCLOPENTANE WITH ALUMINUM CHLORIDE AT 100.0 ± 1.0°

Expt.	C_6H_{12}		Al_2Cl_6 M. × 10^3	Time, hr.	MCP/CH I. R.[b]	Mole, %					
	Iden.	M. × 10^3				C_5H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{14}	C_8H_{16}	C_9H_{18}
18[e]	CH	46	0.16	8.0	0.475	<0.05	0.1[a]	0.1	0.004	0.004	<0.003
19[e]	CH	46	.18	24.0	.485	< .05	.1[a]	0.5	.005	.010	< .003
20[e]	MCP	44	.17	24.0	.503	< .05	< .05[a]	1.0	.05	.10	
21	CH	46	.22	24.0	.509	....	.....	...	....	....	.....
22	CH	46	.17	24.0	.514	....	.....	...	....	....	.....
23	MCP	44	.21	24.0	.530	....	.....	...	....	....	.....
					0.503 ± 0.015						

[a] C_4H_{10} found to be less than 0.5 mole.%. [b,c,d] See notes of Table I. [e] Product recovered by distillation. Over 99.7%w hydrocarbon recovered. [f] See notes of Table I.

deep brown), so that the formation of a colorless aluminum chloride–hydrocarbon complex from the C_6 cyclanes is unexpected. In this regard it must be noted that the aluminum bromide–cyclopentane solutions at 100° give rise to two liquid phases and the more dense phase has a deep brown color.

Discussion

In discussing the methylcyclopentane–cyclohexane equilibrium, two related subjects must be considered along with the ratio of the pair of isomers. These are (1) the possibility of cyclopropane and cyclobutane isomers of C_6H_{12} being present in the system, but undetected due to inadequacy of the analytical methods, and (2) the effect of side reactions on the apparent equilibrium ratio.

It has been reported[2] that dimethylcyclobutanes were found in a low boiling fraction resulting from the action of moist aluminum bromide on cyclohexane at a temperature less than 100°. There

TABLE IIIb

REACTION OF CYCLOHEXANE AND METHYLCYCLOPENTANE WITH ALUMINUM CHLORIDE AT 100.0 ± 1.0°

Expt.	24[a]	25[a]	26	27[a]
C_6H_{12}	CH	MCP	CH	MCP
C_6H_{12} moles × 10^3	46	44	46	44
Time, hr.	33	33	8	8
Wt. % HC recovered	63.7	63.4	82.5	82.0
Al_2Cl_6 moles × 10^3	2.8	2.7	2.3	2.6
Compn. of recovered HC,[b] mole %				
C_3H_8	0.7	0.6	0.2	0.2
C_4H_{10}[c]	14.4	13.6	3.7	4.5
C_5H_{12}[c]	3.2	4.0	1.4	1.5
C_5H_{10}	< 0.1	< 0.1	< 0.05	< 0.05
C_6H_{14}[d]	11.7	9.5	8.1	7.5
C_6H_{12}	61.2	61.1	81.8	82.5
C_7H_{16}	< 0.1	< 0.1	< 0.1	< 0.1
C_7H_{14}	3.6	4.2	1.6	1.6
C_8H_{16}	4.9	6.6	2.6	2.4
C_9H_{18}	0.3	0.4	0.02	0.08
MCP/CH	0.50	0.49	0.50	0.48

[a] Composite of two identical, parallel runs. [b] Combined analytical distillation and mass spectrometric analysis. [c] Predominantly the "iso" isomer. [d] 2 MP, 3 MP, 2.3 M_2B, and 2.2 M_2B identified.

TABLE IV

REACTION OF CYCLOPENTANE WITH ALUMINUM BROMIDE AT 100°

Expt. no.	28	29	30	31	32
C_5H_{10} moles × 10^3	52.3	51.5	51.3	41.6	29.1
Al_2Br_6 moles × 10^3	1.08	1.05	1.00	0.97	1.12
Time, hr.	21	8.0	8.0	161	161
Wt. % volatile	97.4	99+	99+	93.6	94.8
Volatile product					
Mole % C_3H_8	<0.1[a]	....	....	....	....
C_4H_{10}	1.3	....	....	1.6	1.7
C_5H_{12}	3.0	0.14	0.16	2.3	2.2
C_5H_{10}	90.8	99+	99+	91.9	93.0
C_6H_{14}	0.4	<0.05	<0.05	0.1	0.1
C_6H_{12}	4.0	0.46	0.31	2.4	1.7
C_7H_{14}	0.2	0.03	0.03	0.5	0.3
C_8H_{16}	0.01	....	....	0.7	0.5
$C_{12}H_{22}$	....	....	....	0.5	0.5

[a] Mass spectrometric analysis of distillation cuts. Distillation data, 4.0 mole % <45°, 84.5 mole % 45–55°, 11.5 mole % >55°. Cut 2, 45–55°, contained 99.1 mole % C_5H_{10}.

are sound thermodynamic reasons for doubting the identification. From the strain energies suggested by Golmov,[3] the heat of isomerization of a cyclopentane to a cyclobutane or cyclopropane isomer may be calculated to be 31.5 ± 3 kcal./mole. If one takes as a very liberal estimate the corresponding entropy of isomerization to be 20 e.u. (cyclohexane → methylcyclopentane, $\Delta S^\circ = 8.5$ e.u.), the free energy of isomerization at 400°K. is found to be of the order of 20 to 25 kcal./mole. Such a free energy corresponds to an equilibrium ratio of the cyclopropane or cyclobutane isomer to the cyclopentane of less than 10^{-4}, *i.e.*, less than 0.01%.

It is unlikely that direct mass spectrometric or infrared spectrophotometric analysis would be capable of detecting less than 1% of the cyclopropane and cyclobutane isomers of C_6H_{12} in a mixture of cyclohexane and methylcyclopentane plus small quantities (<2%) hexanes and other paraffins and naphthenes, even if the spectra of the twelve isomers were available. Although the spectra of the C_6H_{12}, cyclopropanes, and cyclobutanes have not been measured, it may be predicted that their mass and infrared spectra are such that the two analytical methods will err in the same direction, namely, that the methylcyclopentane will be overestimated and the cyclohexane underestimated in proportion to the quantity of the other isomers in the system. From the estimate of the probable equilibrium concentration of these extra isomers it appears that the analytical error from this source should be negligibly small.

The experiments with cyclopentane were undertaken in part because there is good reason to believe that the presence of methylcyclobutane and the cyclopropane isomers of C_5H_{10} can be detected by means of the mass spectrometer, even though the mass spectra have not been measured. By analogy with the mass spectra of the C_6 and C_7 naphthenes[4] that have been measured, it may be concluded that the relative intensity of the ion $C_4H_7^+$ in the mass spectra of the C_5H_{10} cyclopropanes and methylcyclobutane should be much greater than the relative intensity of this ion in the mass spectrum of cyclopentane. Thus the evaluation of the relative intensity of this ion, $C_4H_7^+$, should provide a sensitive indication of the presence of isomers of cyclopentane.

After correction for the pentane and butane contribution to the mass spectrum of the low boiling (<45°) fraction of the product of experiment 28, Table IV, the residual intensity of the ion, $C_4H_7^+$, relative to that of the ion, $C_5H_{10}^+$, agreed with that characteristic of pure cyclopentane to better than 1%. This fact, combined with the known low boiling points of the isomers of cyclopentane, a conservative assumption concerning the relative intensity, $C_4H_7^+/C_5H_{10}^+$, in that mass spectra of the isomers of cyclopentane, and the analytical data given in the footnote to Table IV, lead to 0.006% as an upper limit to the concentration of isomers of cyclopentane in the product of experiment 28.

The agreement between the calculated and experimental estimates of the upper limit to the concentration of C_3 and C_4 cyclanes which may exist in such systems as those considered in this paper, may be taken as reasonable grounds for ignoring possible effects of such isomers on the accuracy of the determination of the methylcyclopentane–cyclohexane ratios.

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(3) Golmov, *J. Gen. Chem. USSR*, **11**, No. 5-6, 405 (1940). Strain energies per CH_2 group, C_3 ring 11.4, C_4 ring 8.5, C_5 ring 0.5, C_6 and higher rings 0.0 kcal./mole.

(4) The substances which have been studied include methylcyclopentane, cyclohexane, methylcyclohexane, ethylcyclopentane, four of the five dimethylcyclopentanes and a mixture of dimethylcyclohexanes (hydrogenated commercial xylene).

The effect of irreversible side reactions on the apparent equilibrium ratio of a pair of reversibly interconvertible substances has been considered by Bates.[5] His equation (8) for the limiting ($t = \infty$) ratio of B/A for the reacting system (1)

$$\text{(1a)} \qquad A \underset{kb_1}{\overset{ka_1}{\rightleftarrows}} B,\ K\text{ eq} = \frac{B}{A} = \frac{ka_1}{kb_1}$$

$$\text{(1b)} \qquad A \xrightarrow{ka_2} \text{Products}$$

$$\text{(1c)} \qquad B \xrightarrow{kb_2} \text{Products}$$

may be transformed to the form

$$\text{(2)} \qquad \left(\frac{B}{A}\right)_{t=\infty} = \frac{K_{\text{eq}}}{2}\left[\theta + \sqrt{\theta^2 + \frac{4}{K_{\text{eq}}}}\right]$$

where $\theta = 1 - 1/K_{\text{eq}} + (ka_2 - kb_2)/ka_1$. The term $(ka_2 - kb_2)/ka_1$, of the parameter θ, is particularly convenient for estimating the effect of the irreversible side reactions on the apparent equilibrium ratio, $(B/A)_{t=\infty}$. It has been found useful to prepare a graph of $(B/A)_{t=\infty}$ a function of $(ka_2 - kb_2)/ka_1$, for various values of K_{eq}.

Bates has pointed out that if $ka_2 = 0$ and $kb_2 = 0$, his equation (8) reduces to $(B/A)_{t=\infty} = K_{\text{eq}}$. However, the much less stringent condition, $ka_2 = kb_2$, is also a sufficient condition for the equality of the apparent equilibrium ratio, $(B/A)_{t=\infty}$, and the true equilibrium constant for the reversible reaction. In fact, examination of our equation (2) reveals that the important condition, necessary for the equality of $(B/A)_{t=\infty}$ and K_{eq} is that the ratio of the difference between the rates of the irreversible side reactions to the rate of the forward step of the reversible reaction be small compared with $1 - (1/Ke)$.

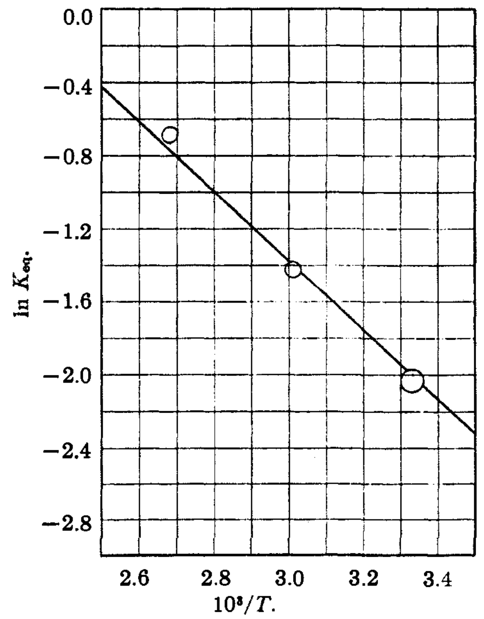

Fig. 1.—The temperature dependence of K_{eq} = methylcyclopentane/cyclohexane.

For the experiments described in Tables I, II, and IIIa, it is apparent that the extent of the irreversible side reactions accompanying the C_6H_{12} isomerization must have had a negligible effect on the ratio of methylcyclopentane to cyclohexane. However, this is not the case for the experiments of Table IIIb. If it is assumed that the kinetics of the reactions of cyclohexane and methylcyclopentane may be represented by the differential equations corresponding to equations (1a), (1b), and (1c), experiments 26 and 27 (Table IIIb) lead to $ka_2 = 0.025$ hr.$^{-1}$, while experiments 24 and 25 give $ka_2 + kb_2 = 0.015$ hr.$^{-1}$. Experiments 18 and 19 in the presence to $^1/_{16}$ the quantity of catalyst present in experiments 24 through 26 indicate $ka_1 \left(\text{CH} \xrightarrow{ka_1} \text{MCP}\right)$ to be of the order of 0.1 hr.$^{-1}$. Thus for experiments 24 through 26 $(ka_2 - kb_2)/ka_1 < 0.02/16 \times 0.1 \cong 0.013$, and $\theta - 1 + 1/Ke_2 < 0.01$, and the ratio of MCP/CH must differ from the equilibrium ratio by less than 0.5% as a result of the side reactions.

In view of the foregoing discussion, it is reasonable to assume that the MCP/CH ratios given in Tables I, II, and IIIa may be taken to be equal to the equilibrium constant for the reaction

$$\text{Cyclohexane (liquid)} \rightleftarrows \text{Methylcyclopentane (liquid)}$$

The three values of this equilibrium constant are shown on the usual ln K vs. $1/T$ plot in Fig. 1. The radii of the circles representing the experimental points are equal to the mean deviations of the individual determinations of the MCP/CH ratio from the averages shown in the tables referred to. The straight line shown on the graph, represented by the equation $\ln K = 4.31 - 1890/T$, is a least squares fit of published values of the equilibrium constant.[1] Our values of the equilibrium constant at 27 and 59° agree within their experimental error with the previous determinations. However, our value for the equilibrium constant at 100° is definitely higher than that indicated by previous determinations. A least squares treatment of our data yields the equation

$$\ln K = 4.814 - 2059/T$$

The heats of combustion of cyclohexane and methylcyclopentane have been measured by Moore and Parks,[6] from which one obtains $\Delta H_{298.1} = 3{,}930 \pm 35$ cal./mole. Aston[7] gives $S^\circ_{298.1}$ (liq. CH) = 48.73 e.u., and Ruehrwein and Huffman[8] found $S^\circ_{298.1}$ (liq. CH) = 48.84 e.u. Douslin and Huffman[9] have recently redetermined the entropy of methylcyclopentane and give $S^\circ_{298.1}$ (MCP liq.) = 59.22 e.u. From the data of these authors one then finds

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[5] Bates, This Journal, **68**, 511 (1946).

[6] Moore and Parks, *ibid.*, **61**, 2561 (1939).

[7] Aston, Szasz and Fink, *ibid.*, **65**, 1135 (1943).

[8] Ruehrwein and Huffman, *ibid.*, **65**, 1620 (1943).

[9] Douslin and Huffman, *ibid.*, **68**, 173 (1946).

$$\text{CH (liq.)} = \text{MCP (liq.)} \quad \Delta H^\circ_{298.1} = 3{,}930 \pm 35 \text{ cal./mole}$$
$$\Delta S^\circ_{298.1} = 10.44 \pm 0.3 \text{ e. u.}$$
$$\Delta C^\circ_{p298.1} = 0.6 \text{ cal./mole } ^\circ\text{K.}$$

The values of ΔH°_{298} and ΔS°_{298} obtained from the equilibrium data are compared with the thermochemical and third law values in Table V.

TABLE V

THE HEAT AND ENTROPY OF THE REACTION CYCLOHEXANE (LIQUID) ⇄ METHYLCYCLOPENTANE (LIQUID) 25°

	Thermal[a]	Equil.[b]	Equil.[c]
$\Delta H^\circ_{298.1}$	3,930 ± 35	3,735	4,015 ± 550
$\Delta S^\circ_{298.1}$	10.44 ± 0.3	8.49	9.50 ± 1.1

[a] See text. [b] ln $K = 4.31 - 1890/T$, from previous investigations. [c] ln $K = 4.814 - 2059/T$, this investigation.

The values of ΔH and ΔS from the equilibrium data have been corrected from an average temperature of 65° to 25° by use of the value of ΔC_p for the reaction quoted above ($\Delta C_p = 0.6$). The values deduced from our data are in considerably better agreement with the thermal data than are those resulting from the averaging over-all previous work.

The assignment of the formula $C_{12}H_{22}$ to the primary high molecular weight product is based on previous identification of dicyclohexyl and dimethyl dicyclopentyl among the reaction products[10] and our observation of an ion of molecular weight 166 in the mass spectra of the products of a number of our experiments.

In view of the rapid coloration upon exposure to air of the non-volatile catalyst complex formed in the reactions at 100°, it seems likely that unsaturated hydrocarbons are present in the catalyst complex. That the "polymer" can act as a hydrogen donor is indicated by the observation that the total quantity of paraffins formed in experiments no. 26 and 27 exceeds one-half of the $C\ H_{12}$ lost as heavy ends.

Our inability to detect cyclopentane in the product of any of the experiments with cyclohexane and methylcyclopentane indicates that reactions between naphthenes, analogous to the well-known paraffin dismutation reactions, are slow.

The results of the experiments with cyclopentane (Table IV) show this substance is not inert to the action of the aluminum halides,[11] although it is considerably less reactive than the C_6 naphthenes. It was definitely surprising to find evidence (mass spectra) for the presence of $C_{12}H_{22}$ (dicyclohexyl, dimethyl dicyclopentyl, etc.) but none for the $C_{10}H_{18}$ (dicyclopentyl). However, the observation that the catalyst complex formed in the cyclopentane reaction is highly colored and similar in appearance to that formed by the action of aluminum halides on paraffins, while the catalyst complex formed from the C_6 naphthene is colorless (in absence of air) indicates that the reactions of the cyclopentane are in important respects different from those of the C_6 naphthenes.

In experiment no. 28 (Table IV) the cyclopentane used was not treated with moist aluminum chloride prior to use. Analyses indicated the sample to contain *ca.* 0.2% cyclopentadiene (ultraviolet) and *ca.* 0.1% cyclopentene (mass spectrometer). The much greater extent of reaction in this experiment than in the other experiments with cyclopentane which had been treated to remove last traces of unsaturates indicates that unsaturates are promoters of catalytic activity in aluminum bromide for reactions of cyclanes. Pines and Wackher[12] have shown that olefins are promoters of isomerization activity in the aluminum halides toward the butanes. Thus there is further evidence of the similarity between the catalysis of alkane and cyclane reactions in the presence of aluminum halides (see the preceding paper).

Summary

The equilibrium constant of the reaction

$$\text{cyclohexane (liq.)} \rightleftarrows \text{methylcyclopentane (liq.)}$$

has been measured at 27, 59 and 100°. It is represented by ln $K = 4.814 - 2059/T$, which corresponds to $\Delta H^\circ_{298.1} = 4015 \pm 550$ cal./mole and $\Delta S^\circ_{298.1} = 9.50 \pm 1.1$ e.u. in good agreement with thermochemical and cryogenic measurements.

Among the products of side reactions accompanying the equilibration in the presence of moist aluminum halides, there have been identified by mass spectrometric analysis, propane, butane, pentane, hexane, C_7, C_8, and C_9 naphthenes and C_{12} binaphthenes. No evidence could be found for the formation of cyclopentane or C_7 or higher alkanes.

Arguments against the formation of C_5 or C_6 cyclopropanes and cyclobutanes from cyclopentane or methylcyclopentane and cyclohexane are presented, and partial experimental confirmation of the arguments is reported.

It has been found that butane, pentane, hexane, C_6, C_7, and C_8 naphthenes and C_{12} binaphthene are formed by the action of moist aluminum bromide on cyclopentane at 100°.

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[10] Ipatieff and Komarewsky, THIS JOURNAL, **56**, 1926 (1934).

[11] Compare Cox, *Bull. soc. chim.*, [4] **37**, 1549 (1925).

[12] Pines and Wackher, THIS JOURNAL, **68**, 595 and 599 (1946).