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The Thermodynamic Properties of C_9H_{18} Naphthenes. I. The Determination of the Equilibrium Constants for the Hydrogenation of Propyl- and Isopropylbenzene and Ethyltoluenes

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The equilibria for the hydrogenation of *n*-propylbenzene, isopropylbenzene, 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, and 1-methyl-4-ethylbenzene were determined experimentally over the temperature range of 250 to 450 °C and under hydrogen pressures ranging from 5 to 50 atm. The data were then used to calculate the values of the free energy and the equilibrium constant of the above reactions and the values of standard free energy of formation from the elements for *n*-propylcyclohexane, isopropylcyclohexane, 1-methyl-*cis*-2-ethylcyclohexane, 1-methyl-*trans*-2-ethylcyclohexane, 1-methyl-*cis*-3-ethylcyclohexane, 1-methyl-*trans*-3-ethylcyclohexane, 1-methyl-*cis*-4-ethylcyclohexane, and 1-methyl-*trans*-4-ethylcyclohexane.

This paper will present the results of a study of the thermodynamic properties of C_9H_{18} naphthenes. Alkylbenzenes are known to react with hydrogen to form alkylcyclohexanes, and the equilibrium constant for the hydrogenation of *n*-propylbenzene(NPB) to *n*-propylcyclohexane (NPCH) can be calculated from the thermodynamic data.[1-3] Such free energy data are available for other C_9H_{12} alkylbenzenes, but not for other C_9H_{18} alkylcyclohexanes. The hydrogenation equilibrium constants have also been determined experimentally over the temperature range from 200 to 300 °C for NPB,[4] isopropylbenzene (IPB),[5] and 1,3,5-trimethylbenzene.[6]

The equilibrium constants for the hydrogenation of NPB, IPB, 1-methyl-2-ethylbenzene (1,2-MEB), 1-methyl-3-ethylbenzene (1,3-MEB), and 1-methyl-4-ethylbenzene (1,4-MEB) were determined over the temperature range from 250 to 450 °C.

From these data, the values of the free energy of formation from the elements were calculated for NPCH, isopropylcyclohexane (IPCH), 1-methyl-*cis*-2-ethylcyclohexane (*cis*-1,2-MECH), 1-methyl-*trans*-2-ethylcyclohexane (*trans*-1,2-MECH), 1-methyl-*cis*-3-ethylcyclohexane (*cis*-1,3-MECH), 1-methyl-*trans*-3-ethylcyclohexane (*trans*-1,3-MECH), 1-methyl-*cis*-4-ethylcyclohexane (*cis*-1,4-MECH), and 1-methyl-*trans*-4-ethylcyclohexane (*trans*-1,4-MECH).

These compounds are important as constituents of petroleum; hence, their properties should have considerable practical interest.

Experimental

Materials. The NPB and IPB used in these experiments were commercial, extra-pure-grade reagents and were purified by distillation in a vacuum in a helium atmosphere to give a product found by gas chromatography to be 100.0% pure. The NPCH (100.0% purity)and IPCH (99.9% purity) were obtained by the hydrogenation of NPB and IPB respectively. The *n*-octane (98% purity), 1,2-MEB (100.0% purity), 1,3-MEB (100.0% purity), and 1,4-MEB (100.0% purity) were commercial, extra-pure-grade reagents and were used without further purification. The *cis*-1,2-MECH, *trans*-1,2-MECH, *cis*-1,3-MECH, *trans*-1,3-MECH, *cis*-1,4-MECH, and *trans*-1,4-MECH were obtained from the *cis-trans* mixtures of 1,2-MECH's 1,3-MECH's and 1,4-MECH's produced by the hydrogenation of 1,2-MEB, 1,3-MEB, and 1,4-MEB respectively, using a Perkin-Elmer F21 Preparative Gas Chromatograph. Hydrogen gas was passed through a palladium catalyst column to remove the oxygen, and the resulting gas was dried with an ice bath as well as with a molecular sieve and silica gel.

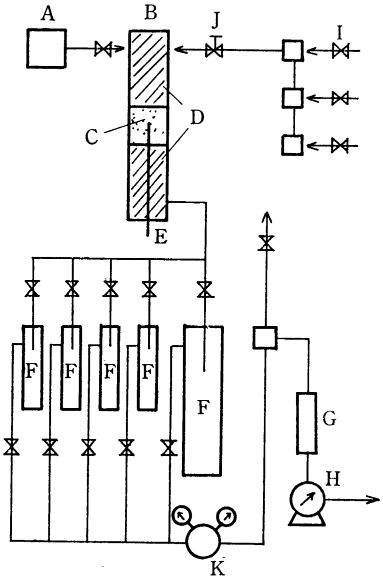


Fig. 1. Schematic diagram of reaction apparatus.
A: feed pump B: reactor C: catalyst bed
D: stainless steel bead E: thermocouple F: separator
G: flowmeter H: gasmeter I: stop valve
J: needle valve K: pressure controller

Apparatus. A flow diagram is shown in Fig. 1. 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 catalyst temperature was measured by means of a chromel-alumel thermocouple located in a thermowell in the catalyst bed. The hydrocarbon feed rates were measured by means of a microfeed pump (Tamaseiki Co.).

The catalyst used in the present experiments was a 5 ml portion of Ketzenfine's 3% platinum on alumina (20—50 mesh). Each feed was a mixture of alkylbenzene and *n*-octane, or of alkylcyclohexane and *n*-octane. The hydrocarbon mixture feed was 1.2 ml per hr, and the mole ratio of hydrogen to the hydrocarbon mixture at the start was 17.8±0.3.

The temperature variation through the catalyst bed was less than 0.5 °C when no reaction was taking place. During a run, the temperature rise due to the heat of reaction was less than 1 °C, depending on the extent of the reaction. The maximum variation in temperature through the catalyst bed during a run was usually of the order of 0.5 °C. The temperature used in the calculations was the average temperature of the last half of the catalyst bed.

A strain gauge (Kyowa Dengyo Co.) was used to measure the pressure at the inlet and outlet of the reactor. The pressure drop across the bed was negligible in the present experiments.

The reactions were carried out at temperatures ranging from 250 to 450 °C and under pressures ranging from 5 to 50 atm. In order to allow time for representative samples to be taken, the first hour was discarded.

Analysis. The products were analyzed by gas chromatography using a Hitachi Model K-53 with flame-ionization detectors and with a squalane capillary column (90 m × 0.25 mm) at 80 °C. The peak areas were measured with a Takeda Model TR-2215 electronic integrator.

Procedure

The hydrogenations of NPB, IPB, 1,2-MEB, 1,3-MEB, and 1,4-MEB are given by the following equations:

	Designation of Equilibrium Constant	
$3H_2(g) + NPB(g) = NPCH(g)$	*K*(n)	(1)
$3H_2(g) + IPB(g) = IPCH(g)$	*K*(i)	(2)
$3H_2(g)$ + 1,2-MEB(g) = *cis*-1,2-MECH(g)	*K*(*cis*-1,2-MECH)	(3)
$3H_2(g)$ + 1,2-MEB(g) = *trans*-1,2-MECH(g)	*K*(*trans*-1,2-MECH)	(4)
$3H_2(g)$ + 1,2-MEB(g) = equilibrium mixture of *cis*- and *trans*-1,2-MECH(g)	*K*(1,2-MECH)	(5)
$3H_2(g)$ + 1,3-MEB(g) = *cis*-1,3-MECH(g)	*K*(*cis*-1,3-MECH)	(6)
$3H_2(g)$ + 1,3-MEB(g) = *trans*-1,3-MECH(g)	*K*(*trans*-1,3-MECH)	(7)
$3H_2(g)$ + 1,3-MEB(g) = equilibrium mixture of *cis*- and *trans*-1,3-MECH(g)	*K*(1,3-MECH)	(8)
$3H_2(g)$ + 1,4-MEB(g) = *cis*-1,4-MECH(g)	*K*(*cis*-1,4-MECH)	(9)
$3H_2(g)$ + 1,4-MEB(g) = *trans*-1,4-MECH(g)	*K*(*trans*-1,4-MECH)	(10)
$3H_2(g)$ + 1,4-MEB(g) = equilibrium mixture of *cis*- and *trans*-1,4-MECH(g)	*K*(1,4-MECH)	(11)

The equilibrium constant, *K*, is given by this equation:

$$K = f_A / f_H{}^3 f_B$$
$$= [(X_A + X)(1-3X)^3 / (X_B - X)(X_H - 3X)^3] K_\gamma P^{-3} \quad (12)$$

where

f_H, f_A, f_B = the fugacities of hydrogen, alkylcyclohexane, and alkylbenzene respectively

X_H, X_A, X_B = the mole fractions of the hydrogen, alkyl cyclohexane, and alkylbenzene respectively of the charge

X = the number of moles of alkylcyclohexane formed from 1 mol of the charge. In runs wherein the equilibrium is approached from the alkylcyclohexane side, $-X$ is the number of moles of alkylbenzene formed from 1 mol of the charge

P = the absolute total pressure of the equilibrium mixture at the end of the catalyst bed, atm

$K_\gamma = \gamma_A / \gamma_H{}^3 \gamma_B$

$\gamma_H, \gamma_A, \gamma_B$ = the fugacity coefficients of hydrogen, alkylcyclohexane, and alkylbenzene respectively.

The fugacity coefficient, γ, was calculated with the aid of the concept of corresponding states, using generalized charts. The following equation, developed by Joffe,7) was used to predict the fugacity coefficients of individual components in a gas mixture:

$$\log \gamma_i = \log \gamma_m + (H^\circ - H)(T_{cm} - T_{ci})/2.303RT \cdot T_{cm} + (Z_m - 1)(P_{cm} - P_{ci})/2.303P_{cm} \quad (13)$$

where

γ_i = the fugacity coefficient of the component, *i*, in the mixture

γ_m = the fugacity coefficient of the mixture

H = the molal enthalpy of the mixture at the given temperature and pressure

H° = the molal enthalpy of the mixture at a low pressure at which the gas is ideal

Z_m = the compressibility factor ($Z_m = PV/RT$) for the mixture

T_{ci} = the critical temperature of the pure component, *i*

P_{ci} = the critical pressure of the pure component, *i*

T_{cm} = the pseudocritical temperature of the mixture

P_{cm} = the pseudocritical pressure of the mixture

T = absolute temperature

R = gas constant.

The pseudocritical temperature and pressure of a mixture are sums of the products of the mole fraction of each pure component in terms of its critical temperature and pressure in accordance with the suggestion made by Kay;8)

$$T_{cm} = \sum_i X_i T_{ci} \quad (14)$$

$$P_{cm} = \sum_i X_i P_{ci} \quad (15)$$

where X_i is the mole fraction of the component, *i*.

In the case of hydrogen, the pseudocritical constants recommended by Newton9) were used in place of the experimental critical constants. The values of the critical constants of pure components were taken from the A.P.I. tables.10) The derivatives of the fugacity coefficients of the mixture with respect to the composition variables may be evaluated by considering the fugacity coefficient of the pseudoreduced temperature, $T_{rm}(= T/T_{cm})$, and the pressure, P_{rm} $(= P/P_{cm})$, of the mixture. By using the pseudoreduced temperature and pressure instead of the true reduced temperature and pressure, γ_m was obtained from a generalized fugacity coefficient chart,9) Z_m was read from a generalized compressibility factor chart,11) and $(H^\circ - H)/T_{cm}$ for the mixture was obtained from a generalized enthalpy-pressure chart.11) In the temperature range above $T_{rm} = 1$, the enthalpy correction values read from the chart were multiplied by a correction factor recommended by York and Weber.12)

Results

Tables 1—5 summarize the experimental results and gives the values of the equilibrium constants, *K*, calculated from the data. Figure 2 shows, for the equilibrium between NPB and NPCH, a comparison of the values derived from this report with values reported experimentally by Vvedenskii, Vinnikova, *et al.*4) over the temperature range of 200—300 °C, and with the values calculated from the thermodynamic data of NPB[3)] and NPCH[2)] using the following equation:

$$\Delta G_f^\circ(\text{NPCH}) - \Delta G_f^\circ(\text{NPB}) = \Delta G_h^\circ(\text{n}) = -2.303RT\log K(\text{n}) \quad (16)$$

where $\Delta G_f{}^\circ$(NPCH) and $\Delta G_f{}^\circ$(NPB) are the standard Gibbs energies of the formation of NPCH and NPB respectively, and where $\Delta G_h{}^\circ$(n) is the standard Gibbs energy of the hydrogenation of NPB to NPCH. Most of the runs were made with a NPB feed, the equilibrium being approached from the NPB side. In Runs A-2 and A-9, the equilibrium was approached from the NPCH side. The same results were obtained

Table 1. Experimental data and equilibrium constants for NPCH

Run No.	Compn. of hydrocarbon feed, mol%	Temp., °C	Pressure, atm	Initial mole ratio H_2/feed	Product mol/mol NPCH/NPB	Side reaction mol%	K_r	K(n)
A- 1	9.5% NPB 90.5% Octane	245.2	4.70	18.13	344	0.0	1.01	3.88
A- 2	8.4% NPCH	272.5	4.59	17.64	27.9	0.7	1.01	3.38×10^{-1}
A- 3	9.5% NPB	320.3	4.70	18.02	0.917	1.4	1.01	1.04×10^{-2}
A- 4	9.5% NPB	298.4	10.31	17.78	25.9	0.6	1.02	2.75×10^{-2}
A- 5	9.5% NPB	329.7	10.11	17.78	5.32	1.0	1.02	5.98×10^{-3}
A- 6	9.5% NPB	366.4	10.08	17.54	0.340	1.5	1.02	3.86×10^{-4}
A- 7	9.5% NPB	348.3	50.4	18.02	114	1.0	0.929	9.77×10^{-4}
A- 8	9.5% NPB	364.7	48.4	17.98	31.7	1.2	0.930	3.08×10^{-4}
A- 9	8.4% NPCH	408.6	48.4	17.62	3.35	2.9	0.934	3.27×10^{-5}
A-10	9.5% NPB	443.8	48.4	17.82	0.641	12.2	0.937	6.28×10^{-6}

Table 2. Experimental data and equilibrium constants for IPCH

Run No.	Compn. of hydrocarbon feed, mol%	Temp., °C	Pressure, atm	Initial mole ratio H_2/feed	Product mol/mol IPCH/IPB	Side reaction mol%	K_r	K(i)
B- 1	9.5% IPB 90.5% Octane	245.2	4.70	18.13	237	0.0	1.01	2.68
B- 2	8.4% IPCH	272.6	4.59	17.64	19.6	0.6	1.01	2.37×10^{-1}
B- 3	9.5% IPB	320.3	4.70	18.02	0.689	1.1	1.01	7.32×10^{-3}
B- 4	9.5% IPB	298.4	10.31	17.78	18.2	0.5	1.02	1.98×10^{-2}
B- 5	9.5% IPB	329.7	10.11	17.78	3.83	1.0	1.02	4.37×10^{-3}
B- 6	9.5% IPB	366.4	10.08	17.54	0.245	1.7	1.02	2.78×10^{-4}
B- 7	9.5% IPB	351.0	48.4	17.87	66.7	1.2	0.929	6.48×10^{-4}
B- 8	9.5% IPB	385.6	48.4	17.91	7.34	1.8	0.931	7.14×10^{-5}
B- 9	8.4% IPCH	406.9	48.4	17.85	2.55	3.2	0.934	2.48×10^{-5}
B-10	9.5% IPB	399.8	48.4	17.74	3.56	2.1	0.933	3.47×10^{-5}
B-11	9.5% IPB	423.1	50.4	17.82	1.26	8.3	0.935	1.09×10^{-5}

Table 3. Experimental data and equilibrium constants for 1,2-MECH's

Run No.	Compn. of hydrocarbon feed, mol%	Temp., °C	Pressure, atm	Product 1,2-MECH/1,2-MEB mol/mol		K		
				cis	*trans*	*cis*	*trans*	Total
C- 1	9.5% 1,2-MEB 90.5% Octane	262.1	5.53	8.35	25.7	6.96×10^{-2}	2.14×10^{-1}	2.84×10^{-1}
C- 2	8.4% *cis*-1,2	284.2	5.43	1.78	5.39	1.49×10^{-2}	4.49×10^{-2}	5.98×10^{-2}
C- 3	9.5% 1,2-MEB	304.1	5.44	0.396	1.17	3.30×10^{-3}	9.78×10^{-3}	1.31×10^{-2}
C- 4	8.4% *trans*-1,2	327.9	9.61	0.461	1.26	7.13×10^{-4}	1.94×10^{-3}	2.65×10^{-3}
C- 5	9.5% 1,2-MEB	288.7	10.17	8.32	24.5	1.08×10^{-2}	3.20×10^{-2}	4.28×10^{-2}
C- 6	9.5% 1,2-MEB	327.2	10.13	0.608	1.65	8.01×10^{-4}	2.17×10^{-3}	2.97×10^{-3}
C- 7	9.5% 1,2-MEB	349.5	10.17	0.191	0.507	2.49×10^{-4}	6.61×10^{-4}	9.10×10^{-4}
C- 8	9.5% 1,2-MEB	379.1	10.17	0.0350	0.0882	4.61×10^{-5}	1.16×10^{-4}	1.62×10^{-4}
C- 9	9.5% 1,2-MEB	324.3	50.4	91.9	251	1.04×10^{-3}	2.83×10^{-3}	3.87×10^{-3}
C-10	9.5% 1,2-MEB	388.6	51.3	2.63	6.72	2.96×10^{-5}	7.57×10^{-5}	1.05×10^{-4}
C-11	9.5% 1,2-MEB	423.2	50.4	0.588	1.29	6.63×10^{-6}	1.45×10^{-5}	2.11×10^{-5}

Table 4. Experimental data and equilibrium constants for 1,3-MECH's

Run No.	Compn. of hydrocarbon feed, mol%	Temp., °C	Pressure, atm	Product 1,3-MECH/1,3-MEB mol/mol		K		
				cis	*trans*	*cis*	*trans*	Total
D-1	9.5% 1,3-MEB 90.5% Octane	265.2	4.32	13.8	3.77	2.34×10^{-1}	6.41×10^{-2}	2.95×10^{-1}
D-2	8.4% *cis*-1,3	285.9	4.32	2.76	0.809	4.69×10^{-2}	1.37×10^{-2}	6.06×10^{-2}
D-3	9.5% 1,3-MEB	310.6	10.26	4.92	1.53	6.26×10^{-3}	1.95×10^{-3}	8.21×10^{-3}
D-4	8.4% *trans*-1,3	332.7	10.26	1.19	0.390	1.52×10^{-3}	4.97×10^{-4}	2.02×10^{-3}
D-5	9.5% 1,3-MEB	340.4	10.72	0.803	0.273	8.92×10^{-4}	3.03×10^{-4}	1.20×10^{-3}
D-6	9.5% 1,3-MEB	358.9	10.69	0.223	0.0784	2.51×10^{-4}	8.83×10^{-5}	3.39×10^{-4}
D-7	9.5% 1,3-MEB	348.3	49.4	49.4	17.0	5.62×10^{-4}	1.93×10^{-4}	7.55×10^{-4}
D-8	9.5% 1,3-MEB	408.6	49.4	1.20	0.486	1.37×10^{-5}	5.33×10^{-6}	1.90×10^{-5}
D-9	9.5% 1,3-MEB	443.8	49.4	0.193	0.0854	2.19×10^{-6}	9.72×10^{-7}	3.16×10^{-6}

Table 5. Experimental data and equilibrium constants for 1,4-MECH's

Run No.	Compn. of hydrocarbon feed, mol%	Temp., °C	Pressure, atm	Product 1,4-MECH/1,4-MEB mol/mol		K		
				cis	*trans*	*cis*	*trans*	Total
E-1	9.5% 1,4-MEB 90.5% Octane	267.4	5.81	8.33	24.2	5.83×10^{-2}	1.69×10^{-1}	2.27×10^{-1}
E-2	8.4% *cis*-1,2	278.4	5.81	3.24	9.07	2.26×10^{-2}	6.34×10^{-2}	8.60×10^{-2}
E-3	9.5% 1,4-MEB	293.3	10.49	6.35	17.6	7.55×10^{-3}	2.09×10^{-2}	2.85×10^{-2}
E-4	8.4% *trans*-1,4	322.6	10.47	0.838	2.07	1.00×10^{-3}	2.47×10^{-3}	3.47×10^{-3}
E-5	9.5% 1,4-MEB	346.9	10.69	0.228	0.537	2.56×10^{-4}	6.03×10^{-4}	6.59×10^{-4}
E-6	9.5% 1,4-MEB	382.2	10.59	0.0281	0.0564	3.24×10^{-5}	6.52×10^{-5}	9.75×10^{-5}
E-7	9.5% 1,4-MEB	314.7	50.4	160	407	1.72×10^{-3}	4.38×10^{-3}	6.10×10^{-3}
E-8	9.5% 1,4-MEB	364.7	50.4	7.65	16.8	8.22×10^{-5}	1.80×10^{-4}	2.62×10^{-4}
E-9	9.5% 1,4-MEB	389.5	51.3	2.04	4.03	2.07×10^{-5}	4.09×10^{-5}	6.16×10^{-5}
E-10	9.5% 1,4-MEB	443.3	50.4	0.190	0.293	2.05×10^{-6}	3.15×10^{-6}	5.20×10^{-6}

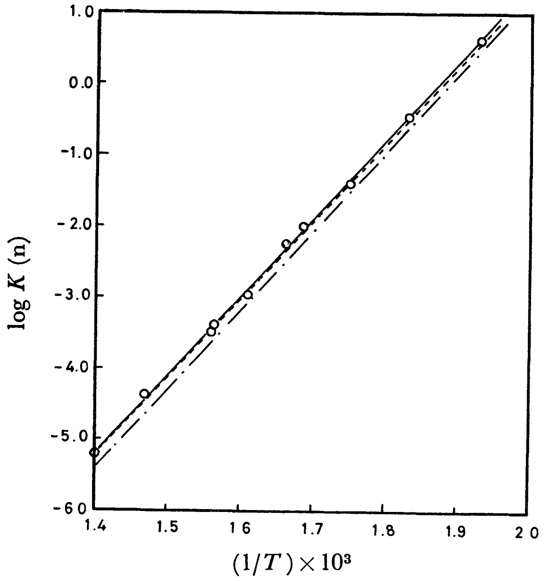


Fig. 2. Logarithn of equilibrium constants for hydrogenation of NPB to NPCH.

○: experimental plot, —·—: calculated from thermodynamic data of NPB and NPCH, ----: reported experimentally by Vvedenskii, Vinikova, *et al.*[4]

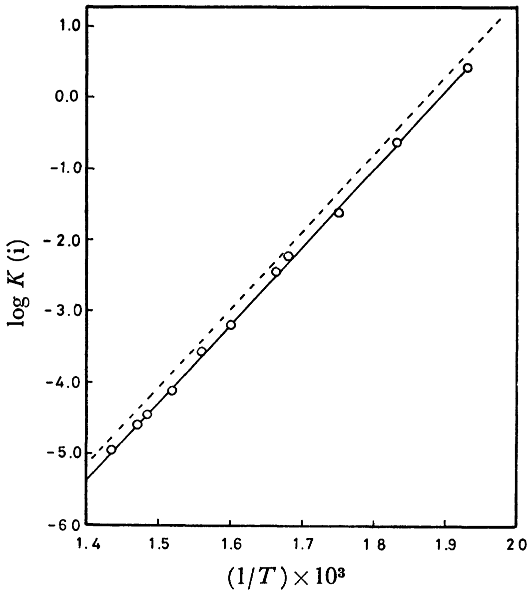


Fig. 3. Logarithm of equilibrium constants for hydrogenation of IPB to IPCH.

○: experimental plot, ----: reported experimentally by Vvedenskii and Takhtareva.[5]

regardless of the side from which equilibrium was approached, thus proving that a true equilibrium was established. Figure 3 shows, for the equilibrium between IPB and IPCH, a comparison of the values derived from this report with those reported experimentally by Vvedenskii and Takhtareva[5] over the temperature range of 204—237 °C.

In Figs. 4, 5, and 6, the values of K for 1,2-MECH's, 1,3-MECH's, and 1,4-MECH's respectively are plotted against $1/T$. Run C-2 was made using a feed containing *cis*-1,2-MECH, but no *trans*-1,2-MECH, while Run C-4 was made using a feed containing *trans*-1,2-MECH, but no *cis*-1,2-MECH. The *cis*-to-*trans* ratio obtained in those experiments is in good agreement with the other results, proving that the hydrogenation product is an equilibrium mixture of the *cis* and *trans* isomers.

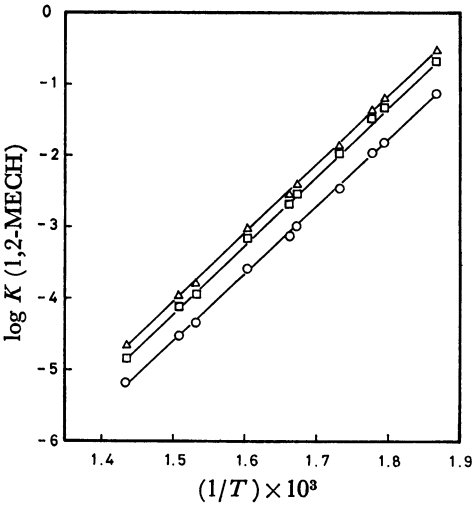


Fig. 4. Logarithm of equilibrium constants for hydrogenation of 1,2-MEB to an equilibrium mixture of *cis*- and *trans*-1-methyl-2-ethylcyclohexanes
○: *cis*-1,2-MECH, □: *trans*-1,2-MECH, △: mixture of *cis*- and *trans*-1,2-MECH's.

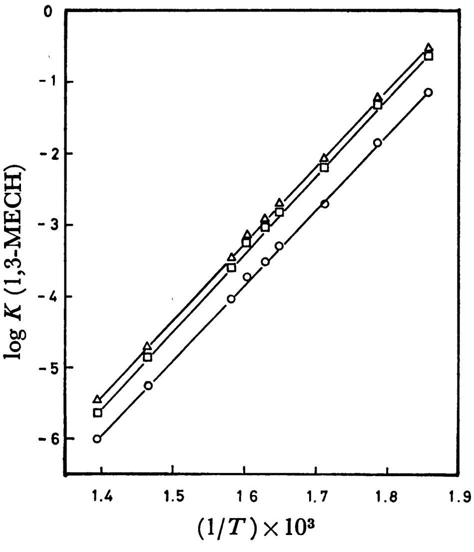


Fig. 5. Logarithm of equilibrium constants for hydrogenation of 1,3-MEB to an equilibrium mixture of *cis*- and *trans*-1-methyl-3-ethylcyclohexanes.
□: *cis*-1,3-MECH, ○: *trans*-1,3-MECH, △: mixture of *cis*- and *trans*-1,3-MECH's.

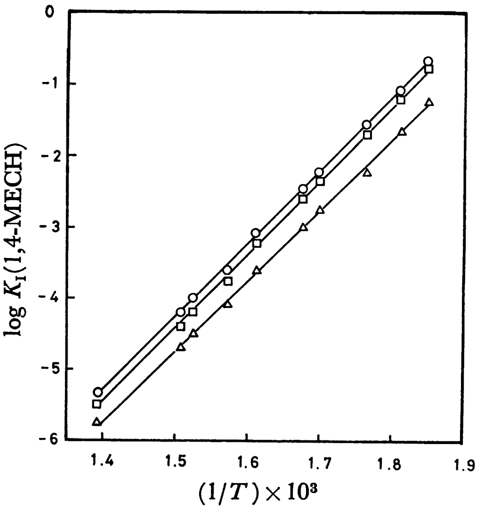


Fig. 6. Logarithm of equilibrium constants for hydrogenation of 1,4-MEB to an equilibrium mixture of *cis*- and *trans*-1-methyl-4-ethylcyclohexanes.
△: *cis*-1,4-MECH, □: *trans*-1,4-MECH, ○: mixture of *cis*- and *trans*-1,4-MECH's.

The following equations for the best straight lines of $\log K$ against $1/T$ were obtained by the least-squares method;

$\log K(\mathrm{n}) = 10975/T - 20.58 \pm 0.03$ (518 to 717 K)
$\log K(\mathrm{i}) = 10887/T - 20.60 \pm 0.04$ (518 to 696 K)
$\log K(\text{1,2-MECH}) = 9536/T - 18.36 \pm 0.04$ (535 to 696 K)
$\log K(\textit{cis}\text{-1,2-MECH}) = 9453/T - 18.82 \pm 0.04$
$\log K(\textit{trans}\text{-1,2-MECH}) = 9651/T - 18.70 \pm 0.04$
$\log K(\text{1,3-MECH}) = 10758/T - 20.51 \pm 0.03$ (538 to 720 K)
$\log K(\textit{cis}\text{-1,3-MECH}) = 10885/T - 20.84 \pm 0.03$
$\log K(\textit{trans}\text{-1,3-MECH}) = 10431/T - 20.56 \pm 0.03$
$\log K(\text{1,4-MECH}) = 10342/T - 19.81 \pm 0.04$ (540 to 716 K)
$\log K(\textit{cis}\text{-1,4-MECH}) = 9993/T - 19.75 \pm 0.04$
$\log K(\textit{trans}\text{-1,4-MECH}) = 10493/T - 20.21 \pm 0.04$

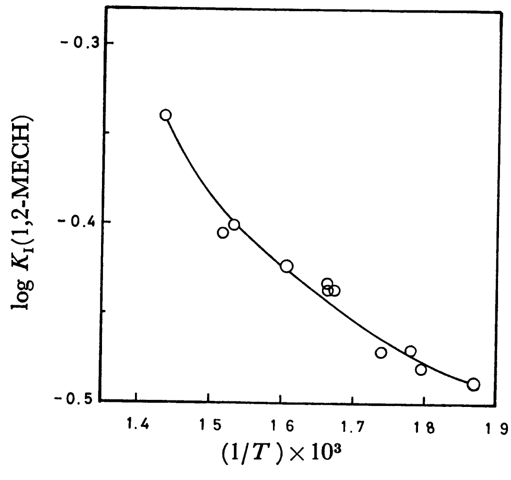


Fig. 7. Logarithm of equilibrium constants of *cis* to *trans* isomerization for 1-methyl-2-ethylcyclohexanes.

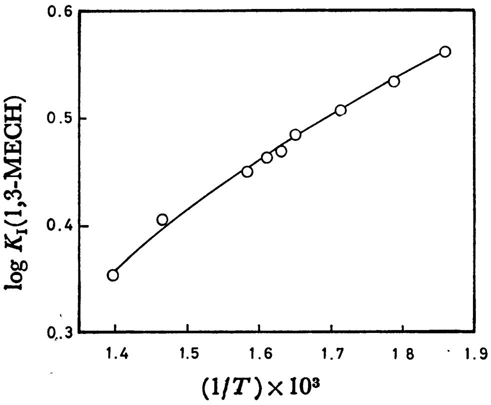


Fig. 8. Logarithm of equilibrium constants of *cis* to *trans* isomerization for 1-methyl-3-ethylcyclohexanes.

From these equations, the standard enthalpy of hydrogenation, $\Delta H_h°$, over the above temperature range for Reactions 1—11 were calculated.

In Figs. 7, 8, and 9 the logarithm of the equilibrium constants of the *cis*-to-*trans* isomerization, K_I, for 1,2-, 1,3-, and 1,4-MECH respectively are plotted against $1/T$.

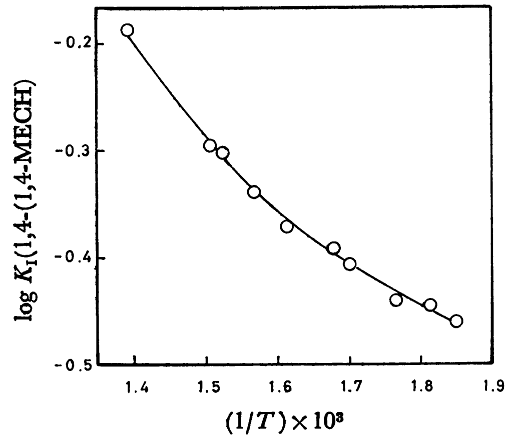


Fig. 9. Logarithm of equilibrium constants of *cis* to *trans* isomerization for 1-methyl-4-ethylcyclohexanes.

Table 6 summarizes the values of $\Delta H_h°$ and of $\Delta G_h°$ calculated by Figs. 2—6 and of $\Delta G_I°$ calculated by Figs. 7—9 over the temperature range from 250 to 450 °C in the ideal gas state.

Table 7 summarizes, for the NPCH, IPCH, and six methylethylcyclohexanes, the values of the standard Gibbs energy of formation, $\Delta G_f°$, calculated from the values of $\Delta G_h°$ and of $\Delta G_f°$ of the corresponding alkylbenzenes,[3] over the temperature range from 250 to 450 °C in the ideal gas state.

TABLE 6. STANDARD ENTHALPIES AND GIBBS ENERGIES FOR REACTIONS 1—11 AND FOR THE THREE *cis* TO *trans* ISOMERIZATION REACTIONS

Compound	$\Delta G°_h$ (kcal/mol)					$\Delta H°_h$ (kcal/mol)
	250 °C	300 °C	350 °C	400 °C	450 °C	
NPCH	−0.96	3.75	8.47	13.18	17.86	−50.2
IPCH	−0.50	4.19	8.92	13.64	18.32	−49.8
1,2-MECH's	0.31	4.51	8.69	12.90	17.10	−43.6
cis-1,2-MECH	1.79	6.08	10.40	14.68	19.02	−43.3
trans-1,2-MECH	0.60	4.88	9.15	13.42	17.72	−44.2
1,3-MECH's	−0.01	4.56	9.23	13.91	18.62	−49.2
cis-1,3-MECH	0.07	4.82	9.61	14.37	19.11	−49.8
trans-1,3-MECH	1.48	6.19	10.89	15.58	20.27	−47.7
1,4-MECH's	0.10	4.64	9.15	13.67	18.22	−47.3
cis-1,4-MECH	1.53	6.06	10.57	15.08	19.61	−45.7
trans-1,4-MECH	0.36	4.98	9.61	14.22	18.85	−46.8
				$\Delta G°_I$ (kcal/mol)		
1,2-MECH	−1.18	−1.22	−1.21	−1.15	(−0.97)[a]	
1,3-MECH	1.38	1.37	1.32	1.26	1.15	
1,4-MECH	−1.13	−1.13	−1.03	−0.84	−0.60	

a) Estimated by extraporated line in Fig. 7.

TABLE 7. STANDARD GIBBS ENERGIES OF FORMATION FOR NPCH, IPCH, AND SIX METHYLETHYLCYCLOHEXANES

Compound	$\Delta G_f°$ (kcal/mol)				
	250 °C	300 °C	350 °C	400 °C	450 °C
NPCH	56.71	67.28	77.87	88.43	98.99
IPCH	57.74	68.43	79.17	89.89	100.57
cis-1,2-MECH	57.90	67.95	78.10	88.27	98.52
trans-1,2-MECH	56.71	66.75	76.85	87.01	97.19
cis-1,3-MECH	54.88	65.38	75.97	86.59	97.25
trans-1,3-MECH	56.29	66.75	77.25	87.80	98.38
cis-1,4-MECH	56.70	67.04	77.42	87.87	98.36
trans-1,4-MECH	55.53	65.96	76.46	87.01	97.60

Discussion

The structural analysis of dimethylcyclohexanes given by Beckett, Pitzer, and Spitzer[13] can be extended to the methylethylcyclohexanes. The stable form of cyclohexane is the chair form. NPCH and IPCH have their propyl groups only in the equatorial position because of the large strain energy in the axial position. A value of 0.8 kcal/mol has been given by Pitzer[14] for the strain energy, *a*, in *n*-butane twisted 120° about the central carbon-carbon bond (*gauche* conformation) as compared to the stable, planar conformation (*trans* conformation) of that molecule; the value of 0.61 kcal/mol is given by Bartell and Kohl.[15] Axial methylcyclohexane has two similar interactions and has been assigned a value of 1.8 kcal/mol, or $a=0.9$ kcal/mol, for the strain energy by Beckett, Pitzer, and Spitzer.[13]

The methylethylcyclohexanes have two isomers: (*cis*-1,2), (*trans*-1,3), and (*cis*-1,4) have one with an axial methyl and an equatorial ethyl group and one with an equatorial methyl and an axial ethyl group, while (*trans*-1,2), (*cis*-1,3), and (*trans*-1,4) have one with both alkyl groups axial and one with both alkyl groups equatorial. These isomers have more three rotational isomers for the ethyl group.

Table 8 summarizes various parameters arising from the isomerism of the methylethyl derivatives. Since *gauche* twists may be either right-handed (G) or left-handed (G′), there are more ways of realizing *gauche* than *trans* conformations. This is reflected in the multiplicity, *m*, listed in Table 8 for each type of isomer. The chair-boat isomerism has been ignored because of the latter's high strain energy.

For *cis*-1,3 derivatives, the axial form encounters much worse steric interference because both alkyl groups are on the same side of the plane. These steric interactions are similar to those of *n*-pentane with the adjacent G and G′ conformations. This type of interference also exsists in rotational isomers with an axial ethyl group. The value of $2a$ given by Beckett, Pitzer, and Spitzer[13] has been assigned to this type of interference.

The calculated values of free energy are found by taking the mixture of isomers denoted in Table 8 and by giving *a* the value of 0.9 kcal/mol. They are in excellent agreement with the values of this report observed at 250 °C.

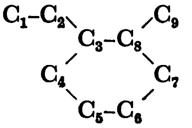
The author gratefully acknowledges helpful discussions with Dr. Toshiaki Kabe, Mrs. Shoko Yamadaya, and Mr. Masaaki Oba during this work.

Table 8. Isomerizm in methylethylcyclohexanes

Compound	Methyl group	Ethyl group	Conform. of ethyl group	m[a]	Energy	*trans/cis*	$\Delta G^{\circ}_{\mathrm{I}}$,[b] kcal/mol Calcd	$\Delta G^{\circ}_{\mathrm{I}}$,[b] kcal/mol Obsd
cis-1,2	ax	e	TTG–TG[d]	2	$4a$			
	ax	e	TTG–GG′	1	$6a$			
	e	ax	GGG–TG	1	$4a$			
	e	ax	GGG–TG′	1	$6a$			
	e	ax	GGG–G′G′	1	$9a$			
trans-1,2	e	e	TTG–GG	1	$3a$			
	e	e	TTG–TG	1	$2a$			
	e	e	TTG–TG′	1	$4a$			
	ax	ax	TGG–TG	2	$5a$			
	ax	ax	TGG–G′G′	1	$10a$	2.94	−1.12	−1.18
cis-1,3	e	e	TT–TG	2	a			
	e	e	TT–GG	1	$2a$			
	ax	ax	G(GG′)–TG	2	$7a$			
	ax	ax	G(GG′)–G′G′	1	—[c]			
trans-1,3	ax	e	TT–TG	2	$3a$			
	ax	e	TT–GG	1	$4a$			
	e	ax	GG–TG	2	$3a$			
	e	ax	GG–G′G′	1	$8a$	0.322	1.18	1.38
cis-1,4	e	ax	GG–TG	2	$3a$			
	e	ax	GG–G′G′	1	$8a$			
	ax	e	TT–TG	2	$3a$			
	ax	e	TT–GG	1	$4a$			
trans-1,4	e	e	TT–TG	2	a			
	e	e	TT–GG	1	$2a$			
	ax	ax	GG–TG	2	$5a$			
	ax	ax	GG–G′G′	1	$10a$	3.17	−1.20	−1.13

a) Multiplicity takes into account right- and left-handed *gauche* twists. b) Values at 250 °C. c) This conformation is considered to be sterically unreasonable and is given zero weight.

d)



C_2 — C^1

T C_2–C_5 T C_1–C_8

T C_2–C_7—G C_1–C_4

G C_2–C_9

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