cyclobutane (XXII) in one liter of dry ether over a period of 48 hours. The reaction mixture was cooled to room temperature and decomposed by the addition of 100 ml. of 2 *N* hydrochloric acid and 50 ml. of 6 *N* hydrochloric acid. Stirring at room temperature next was continued 0.5 hour to hydrolyze the imine.

The water layer was separated, extracted once with ether, and discarded. The volatile material from the combined organic layers was distilled under vacuum and the residue was heated under reflux with 200 ml. of 33% sulfuric acid for 3 hours. The ketone was steam distilled out of the reaction mixture over a period of 24 hours. The distillate was extracted 5 times with ether and the ether extracts were combined, washed with water, and dried over magnesium sulfate. The solvent was removed by fractionation, and the ketone was distilled, b.p. 100–104° (35–40 mm.), $n^{25}\text{D}$ 1.4876, yield 5.0 g. (72%).

Anal. Calcd. for $C_9H_{14}O$: C, 78.26; H, 10.14. Found: C, 78.14; H, 10.04.

The semicarbazone, recrystallized from ethanol–water, gave fluffy needles, m.p. 178–179°. Mixture melting point with the semicarbazone of the *trans* isomer was depressed.

Anal. Calcd. for $C_{10}H_{17}N_3O$: C, 61.54; H, 8.72. Found: C, 61.27; H, 8.77.

cis-**Bicyclo[5.2.0]nonane** (IVa).—The Wolff–Kishner reduction of ketone XIXa was carried out as described for the preparation of the *trans* isomer XIXb. The product was distilled twice, $n^{25}\text{D}$ 1.4662, b.p. 152–155° uncorr. Gas chromatography showed the compound was substantially better than 99% pure.

Anal. Calcd. for C_9H_{16}: C, 87.10; H, 12.90. Found: C, 86.83; H, 12.66.

Equilibration Studies with the Bicyclo[5.2.0]nonanes.—One of the pure isomeric hydrocarbons, in the amount of 100–200 mg., was heated in a small sealed tube with *ca.* 20 mg. of 10% palladium-on-carbon. The results of the equilibration experiment then were determined by vapor phase chromatography. A 10-foot column of tricresyl phosphate on firebrick was used for the separation.

At 133°, where the retention times were 62 and 50 minutes, respectively, for the *cis*- and *trans*-hydrindane, the corresponding times for IV *cis* and *trans* were 69 and 63 minutes.

When the equilibration was carried out with IVb for 48 hours at 250°, the vapor phase analysis showed only a single peak corresponding to the starting isomer. The *cis* isomer IVa showed several % reaction under these conditions, but IVb was absent. At 315° considerable reaction took place with both isomers. From the *trans* isomer of IV (retention time 66 minutes) there was obtained a mixture which showed on vapor phase analysis two principal peaks in a 1:1 ratio with retention times of 65 and 55 minutes. From the *cis* isomer similarly there was obtained a 1:1 mixture with retention times of 70 and 55 minutes. In each case four minor components were detected, with retention times of less than 56 minutes and in total amount less than 5% of the mixture. In no case was any of the isomerized compound detected.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE STATE UNIVERSITY]

The Relative Stabilities of *cis* and *trans* Isomers. VI. The Decalins[1,2]

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The equilibrium constant for the reaction *cis*-decalin ⇄ *trans*-decalin has been measured in the liquid phase under a pressure of hydrogen over the temperature range 531–641°K. From the data the thermodynamic quantities for the isomerization under these conditions were calculated as ΔH^{586} -2.72 ± 0.20 kcal./mole, and ΔS^{586} -0.55 ± 0.30 e.u. The feasibility of this general method for measuring the thermodynamic constants for such a reaction has been established.

Introduction

The relative stabilities of *cis* and *trans* junctures in fused ring systems are of fundamental importance in organic chemistry, and qualitative equilibrium data as well as a few approximate heats of combustion for some simple cases have been available[3] for many years. More recently, with the development of the principles of conformational analysis,[4] a better understanding of these stabilities has been achieved, and a more quantitative knowledge of such systems has become desirable. Such a knowledge of complex systems as are commonly found in nature, for example in the steroids and terpenes, has been and will continue to be a great help in understanding much of the chemistry of these compounds. Conformational analysis enables predictions to be made only with respect to the heat contents of various structures. In order to gain a quantitative understanding of the stabilities of such ring junctures, it is necessary that both the heats and entropies of isomerization be determined for a variety of simple systems. The almost total absence of entropy data for fused ring systems has led usually to the neglect of entropies of isomerization.[5] That this neglect may lead to incorrect conclusions has been pointed out previously.[6]

The thermodynamic functions of an organic compound may be obtained from the heat of combustion together with either spectral or heat capacity measurements. Both methods commonly are used, and they are quite generally applicable and quite accurate though rather laborious. In the present case the real interest lies not in the entropy and heat content of each isomer, but rather in the difference between these quantities for the two isomers. Such differences may in principle be determined from measurements of the equilibrium constant between the isomers as a function of temperature. There appears to be only one earlier attempt in the literature to obtain the thermodynamic quantities from the isomerization of a fused ring system in this way.[7]

The objectives of the present work were both to

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[2] Paper V, THIS JOURNAL, **81**, 4074 (1959).

[3] (a) R. P. Linstead, *Ann. Rep. Chem. Soc.* (*London*), 305 (1935); (b) W. Hückel, "Theoretical Principles of Organic Chemistry," Vol. I, Elsevier Publishing Co., New York, N. Y., 1955, pp. 98–114.

[4] D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953); D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 44 (1956).

[5] R. M. Gascoigne, *J. Chem. Soc.*, 876 (1958).

[6] N. L. Allinger, *J. Org. Chem.*, **21**, 915 (1956).

[7] W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *ibid.*, **19**, 222 (1954).

determine the thermodynamic quantities for the isomerization reaction *cis*-decalin → *trans*-decalin, and to establish the applicability of the method so as to make possible its extension to other important systems for which thermodynamic data are completely unavailable.

Some quantitative data on the decalins were available in the literature at the time this investigation was undertaken[8–10] and additional data have since been reported.[11,12] The early measurements of the heats of combustion of the decalins[8] gave the heat of isomerization[13] as −2.12 kcal./mole. More recently the value −2.69 kcal./mole has been quoted,[12] and probably is more accurate. The calorimetric entropy difference was first reported[9] as +0.96 ± 0.3 e.u. No comment was made on this value by Miyazawa and Pitzer[11] who in their paper gave data from which an entropy difference of –0.03 e.u. can be calculated.

Results

In the present work the equilibrium between the *cis*- and *trans*-decalins was established by heating a mixture rich in one isomer with a palladium catalyst for a suitable length of time as determined by preliminary experiments. Under these conditions the equilibration was brought about by a hydrogenation–dehydrogenation reaction. Equilibrium was approached from both sides at several temperatures over the range from 531° to 641°K. The dehydrogenation reaction proceeds to an inconvenient extent at the higher temperatures, and was suppressed by carrying out the equilibration in a bomb under a pressure of hydrogen on the order of 60 atmospheres. A simple calculation showed that although the high pressure would be expected to shift slightly the point of equilibrium, the error introduced by its neglect was inconsequential.

The composition of the vapor in equilibrium with the liquid at the various temperatures was calculated by extrapolation of the known vapor pressure data[14] using the Antoine equation. It was found that the vapor contained about 1% less of the *cis* isomer than did the liquid throughout the temperature range employed. Using the Berthelot equation with T_c = 681.5°K. and P_c = 27 atm.[15] it was calculated that at the highest temperature used in the equilibrations approximately one-fourth of the decalin was in the gas phase, while at the lowest temperatures the fraction was only about one-twentieth.

This means that the measured *cis* content, which was an average of liquid and gas phase compositions, was less than the true equilibrium point in the liquid phase by an amount that varied from 0.10% at 531° to 0.35% at 641°. These corrections were made, and it was found that the errors which would have been introduced by ignoring them were about 0.1 kcal./mole in ΔH and 0.2 e.u. in ΔS. These amounts are of the order of the experimental error.

To measure with high accuracy the composition of a mixture of decalins before the development of gas phase chromatography would have been a very formidable task. Using this analytical method, it was found that the *trans/cis* ratio varied with temperature from about 6.5 to 10.3, and these numbers were reproducible to about ±0.03. Tetralin was formed by dehydrogenation during the equilibration, but the amount was small and its presence in no way interfered with the analysis. Since all of the compounds are hydrocarbons, the presence of a small amount of tetralin would not be expected to make any significant change in the equilibrium point. A summary of the data is recorded in Table I.

TABLE I

EQUILIBRATION DATA *cis*-DECALIN ⇄ *trans*-DECALIN

t, °K.	% *cis*	Vapor corrn.	% *cis* (liq.)	K^{t}_{liq}
531	8.86	+0.10	8.96	10.161
534	9.16	.10	9.26	9.799
555	10.04	.12	10.16	8.842
560	10.10	.13	10.23	8.775
579	10.83	.18	11.01	8.083
583	11.07	.19	11.26	7.881
609	12.04	.26	12.30	7.130
615	12.23	.27	12.50	7.000
637	12.92	.34	13.26	6.541
641	13.16	.35	13.51	6.402

A plot of ln K against $1/T$ was made and the best line was drawn through the points by the method of least squares. The desired constants were obtained from the intercept at $1/T = 0$ and slope. The values obtained were ΔS^{586} −0.55 ± 0.30 e.u., and ΔH^{586} − 2.72 ± 0.20 kcal./mole. The agreement of ΔH with the more recent of the combustion values (−2.69 kcal./mole[12]) and with the value calculated by conformational analysis (−2.7 kcal./mole[16]) is excellent.

The thermodynamic functions of the decalins[11] offer an opportunity also to compare the entropy of isomerization. The literature values concern the gas phase at the temperatures covered in the present work, but the entropy change of the liquid on isomerization can be found in the following way. The heat capacities of the liquid decalins are accurately known[17] in the range 300–350°K. The equation for the change in heat capacity upon isomerization of *cis*-decalin to *trans*-decalin in cal./mole degree is given[11] as

$$\Delta C_p = \Delta C_1 + \Delta C_2 T$$

where ΔC_1 and ΔC_2 have, respectively, the numerical values −1.73 and +0.0030 over the range 300–350°K. In the absence of other information, this equation can be used for extrapolation of the liquid heat capacity change to the temperature range employed in the present work. The entropy of the isomerization is given by

$$\Delta S = \int (\Delta C_1/T + \Delta C_2)\mathrm{d}T$$

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[8] G. F. Davies and E. C. Gilbert, THIS JOURNAL, **63**, 1585 (1941).

[9] G. S. Parks and J. A. Hatton, *ibid.*, **71**, 2773 (1949).

[10] W. F. Seyer, *ibid.*, **75**, 616 (1953).

[11] T. Miyazawa and K. S. Pitzer, *ibid.*, **80**, 60 (1958).

[12] F. D. Rossini, quoted in ref. 11.

[13] Throughout this paper the signs of the thermodynamic quantities are those for the isomerization in the direction *cis*-decalin → *trans*-decalin, and all numerical values refer to the liquid phase at 25° unless otherwise stated.

[14] D. L. Camin and F. D. Rossini, *J. Phys. Chem.*, **59**, 1173 (1955).

[15] Kamenz, Gross and Tappe, quoted by L. Riedel, *Chem. Ing. Tech.*, **24**, 353 (1952).

[16] Using 0.9 kcal./skew interaction. If 0.8 is used the calculated value is −2.4 kcal./mole.

[17] G. Waddington, quoted in ref. 11.

and the integration constant can be evaluated from the known ΔS at one temperature. The entropy change for the isomerization in the liquid phase calculated in this way was -0.36 e.u. at 586°K., in good agreement with the present experimental value of -0.55 e.u. The earlier value of Parks and Hatton is substantially different.

The symmetry number of each isomer is two, but since the *cis* isomer exists in *d* and *l*-conformations there is predicted for it an entropy of mixing of $R \ln 2$ or, for the isomerization, an entropy change of -1.38 e.u. The experimental value of the entropy difference is somewhat less than this in the liquid phase, which fact suggests more ordering for the *cis* isomer in the liquid. The value of ΔS does, however, show that the ring system is of similar rigidity for each isomer.

Earlier,[6] a rationalization of the stabilities of various decalin and hydrindane ring systems was made based on the assumption that the entropy of a *cis* fused system would be greater than that of the corresponding *trans* isomer. It now appears that with the decalins themselves the *cis* isomer does in fact have a slightly greater entropy, but the difference cannot be ascribed to a difference in flexibility and is too small to explain the discrepancy between the stability of the isomers of 9-methyldecalin as calculated from conformational analysis and as found experimentally[18] for 9-methyl-1-decalone. The 2-alkyl ketone effect proposed by Klyne[19] appears to account adequately for the observed facts in this latter case.

With respect to rigidity, the chair form of the cyclohexane ring is essentially a special case, since evidence for appreciable flexibility has been advanced for the boat form of the cyclohexane ring,[20] and the 4-,[21] 5-,[22] 7-[23] and 8-[24] membered rings. The conclusions reached for the decalins cannot therefore be carried over *a priori* to the hydrindanes, or to other systems of this flexible group.

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Experimental

***cis*- and *trans*-Decalin.**—Pure samples of each isomer were obtained by fractional distillation of one liter of commercial decalin through a 4′ column equipped with a heated jacket and total reflux head and packed with glass helices. Gas phase analysis showed the fraction boiling at 183.9–184.9° (740 mm.), $n^{20}\text{D}$ 1.4697, contained less than 1% of the *cis* isomer while the fraction boiling at 192.0–193.0°, $n^{20}\text{D}$ 1.4810, contained less than 1% of the *trans* isomer. Redistillation of these samples through the same column gave 40 ml. of each isomer containing no impurity detectable by gas phase analysis, and having the properties: *trans*-, b.p. 184.5° (747 mm.), $n^{20}\text{D}$ 1.4697; *cis*-, b.p. 192.7–193.5° (743 mm.), $n^{20}\text{D}$ 1.4811. The reported constants are[25] *trans* $n^{20}\text{D}$ 1.4697 and *cis* $n^{20}\text{D}$ 1.4812.

Equilibration.—The equilibrium was approached from each side at approximately the same temperature as will be described. Twenty ml. of decalin which was a mixture of the two isomers well to one side of the equilibrium point was placed in a 100 ml. Magna-Dash hydrogenation bomb together with 0.4 g. of 5% palladium-on-carbon. The bomb was flushed twice with 500 lb. of hydrogen, a hydrogen pressure of 500 lb. then was introduced, the system was closed off and heating and stirring were started. The bomb contents were stirred and maintained at the desired temperature (±5°) for a sufficient time to reach equilibrium; this time varied from about 40 hours at 530°K. to 6 hours over 600°K. The temperature was held more constant (±1°) for the final few hours of the equilibration period. The temperature was measured with a Leeds and Northrup calibrated potentiometer using an iron–constantan thermocouple inserted in a well in the bottom of the bomb. It was determined that the temperatures measured in this way were within 1° of the temperatures inside the bomb. After equilibrium was established the stirrer was turned off and the catalyst was allowed to settle for a few minutes. The bomb then was pulled from the heating jacket and plunged into an ice-bath. After releasing the hydrogen pressure the bomb was opened, and the decalin was filtered through Celite to remove the catalyst.

Analysis.—Various columns were tried for the gas phase chromatographic analysis. Dioctyl phthalate on firebrick and Apiezon grease on Florex gave a fair separation. The tris-β-cyanoethylation product of glycerol on Florex gave sharp rather well separated peaks initially, but the separation deteriorated rather rapidly with column use. The column finally used was made by suspending commercial tricresyl phosphate on 50–60 mesh Florex in a 3:5 ratio. Firebrick also was used as a support, and gave the same results as did Florex. The length of the column was 10 feet.

The gas analysis was carried out at 173° using a 0.04-ml. sample, and retention times on the column were about 64 and 80 min. for the *trans* and *cis* isomers, respectively, and 167 min. for tetralin. Separation was substantially complete. The ratio of isomers in the mixture was taken as equal to the ratio of the products of the band height and half-band width as determined graphically. For maximum accuracy all of the equilibrated samples together with a known mixture of decalins containing 10.04% *cis* isomer were run consecutively. The known sample gave 9.35, 9.52, 9.43 and 9.42% *cis*. A correction factor of +0.61% was therefore added to the measured percentage of *cis*-decalin for each analysis.[26] Each sample was analyzed at least twice, and the percentages of each isomer found in duplicate analyses usually agreed within 0.03. The random errors in the measured free energies thus varied from about ±8 cal. at 520° to ±5 cal. at 640°K.

The values of ΔH and ΔS for the reaction *cis*-decalin $\rightleftarrows$ *trans*-decalin were determined from the intercept and the slope of a line drawn by the method of least squares through the points obtained from a plot of $\ln K$ against $1/T$. The values, together with the estimated probable errors, are ΔH^{586} 2.72 ± 0.20 kcal./mole and ΔS^{586} -0.55 ± 0.30 e.u.

The effect of pressure on the isomerization was calculated from the relationship $(\partial \Delta V/\partial P)_T = \Delta V$. Since the equilibrations were all done at a pressure of 800–1000 lb./sq. in., the effect of pressure change and of the pressure itself was negligible.

To find the amount of decalin in the gas phase the Berthelot equation was used, together with the known critical constants.[11,15] The volume of the bomb was 100 ml. and 20 ml. of decalin was used.

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[18] A. Ross, P. A. S. Smith and A. S. Dreiding, *J. Org. Chem.*, **20**, 905 (1955).

[19] W. Klyne, *Experientia*, **12**, 119 (1956).

[20] P. Hazebroek and L. J. Oosterhoff, *Disc. Faraday Soc.*, **10**, 87 (1951).

[21] G. W. Rathjens, Jr., N. K. Freeman, W. D. Gwinn and K. S. Pitzer, THIS JOURNAL, **75**, 5634 (1953).

[22] (a) J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *ibid.*, **69**, 2483 (1947); (b) J. G. Aston, S. C. Schumann, H. L. Fink and P. M. Doty, *ibid.*, **63**, 2029 (1941).

[23] N. L. Allinger, *ibid.*, **81**, 232 (1959).

[24] (a) E. Billeter, T. Bürer and H. H. Günthard, *Helv. Chim. Acta*, **40**, 2046 (1957); (b) T. Bürer and H. H. Günthard, *ibid.*, **40**, 2054 (1957).

[25] W. F. Seyer and R. D. Walker, THIS JOURNAL, **60**, 2125 (1938).

[26] Experiments with other compounds showed that a small correction factor such as this is always necessary for highest accuracy. It appears to be a constant percentage, relatively independent of the composition of the mixture.