$$K_{sp} = [Na^+]^2[Cu^{2+}][Fe(CN)_6^{4-}] = K_t[Cu(P_2O_7)_2^{6-}][Fe(CN)_6^{4-}][Na^+]^2/[P_2O_7^{4-}]^2 \quad (10)$$

The solubility product of sodium copper ferrocyanide[14] was found to be 4.9×10^{-15} at an ionic strength of about unity by an analogous equilibration procedure using 0.25 M sodium oxalate to dissolve sodium copper ferrocyanide through the formation of dioxalatocuprate(II). The instability constant of this complex has been determined by Meites[15] on the basis of the shift of the polarographic half-wave potential of copper ion due to complex formation.[16]

Substituting the value 2.7×10^{-13} for K_t from Table II into equation (8) yields a mean value, 1.6×10^{-9}, for K_{i2}.

The difference in the magnitude of the first and second dissociation constants can be explained on the basis of ionic charge. The first pyrophosphate ion is attracted by the oppositely charged copper ion while the second pyrophosphate ion must combine with a similarly charged monopyrophosphatocuprate(II) ion.

The above value for K_t is supported by the following polarographic evidence. Laitinen and Onstott,[2] as well as Eriksson,[5] showed that the polarographic reduction of the pyrophosphate complex present in the pH range of 2 to 5 is reversible. The beginnings of the waves which were obtained at larger pH's are similar. However, at more negative potentials, the normal current growth discontinues abruptly and an appreciable current decrease may even be observed. The authors, after performing polarographic experiments with solutions containing 10^{-4} to 10^{-2} M copper ion and 10^{-4} to 1 M pyrophosphate ion with similar results, concurred with Eriksson in his opinion that film formation rather than thermodynamic irreversibility was responsible for the strange wave shape. Using Eriksson's technique of extrapolating along the normal beginning of the wave, the authors have obtained the half-wave potential of -0.2451 volt (S.C.E.) for a solution 1 millimolar in $[Cu(P_2O_7)_2]^{6-}$, 8 millimolar in $P_2O_7^{4-}$, 1 M in KNO_3, and 0.003% in gelatin. Combining this data with the experimentally determined value, $+0.002$ v. (S.C.E.), for the half-wave potential of tetraaquocuprate(II),[14] yields a value, 3×10^{-13}, for K_t in excellent agreement with the value 2.7×10^{-13} obtained by equation (10).

COLUMBUS, OHIO

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[14] J. I. Watters, unpublished.

[15] L. Meites, THIS JOURNAL, **72**, 180 (1950).

[16] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, p. 164.

[CONTRIBUTION FROM THE DEPARTMENT OF ENGINEERING, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Heat Capacity of *cis*- and *trans*-Decahydronaphthalene and the Possible Existence of a λ-Region for the *cis* Form at 50.1-50.5°

BY WILLIAM F. SEYER

RECEIVED JUNE 16, 1952

In attempting to measure the heat capacity of *cis*- and *trans*-decahydronaphthalene between 20° and 140° by the Williams and Daniels adiabatic method irregularities in the behavior of the *cis* modification were noted in the temperature interval 50–60°. Heating and cooling caves indicated a discontinuity between 50.1° and 50.4°. By slightly altering the set-up of the calorimeter and adding definite increments of heat, a curve was obtained suggesting a λ-region over this temperature interval. Other physical measurements made on the *cis* isomer appear to support this view.

In making a series of measurements on the physical properties of *cis*- and *trans*-decahydronaphthalene in the liquid state none was found more difficult than that of the heat capacity. This was particularly true for the *cis*-form. Several experiments had shown an irregularity in the case of this compound in respect to change in properties with temperature so that it was deemed desirable to investigate the specific heats of these two compounds in the hope of getting more information on the peculiar temperature behavior of the *cis* isomer. A study of the various calorimetric methods in use resulted in the selection of the Williams and Daniels adiabatic calorimeter type as the most suitable for the purpose in mind.[1] Preliminary measurements to test the operation of this type of calorimeter showed a regular increase in the heat capacities of benzene, toluene and *trans* decahydronaphthalene but not with the *cis* isomer.[2] Here the results were extremely irregular, especially in the neighborhood of 50°. It soon became apparent that in order to be able to reproduce the shape of the curves the utmost care would have to be taken in the experimental procedures. Hence a new calorimeter was constructed after the model mentioned above with special efforts devoted to the minimizing of those errors so thoroughly discussed by W. P. White in his treatise, "The Monern Calorimeter."[3]

Calorimeter Characteristics.—The specific factors which have a bearing on the results obtained are stated briefly below. The stirring in the inner cup gave a temperature rise of not over 0.0001° per minute and was therefore considered to be a negligible quantity. The samples of hydrocarbons used weighed between 150 and 160 g. Prior to each run, the purity of each *cis* or *trans* isomer to be used was tested by measuring the freezing point. The thermel was made from 36 B & S gage copper wire and 30 B & S gage special copel wire. Five couples were used to each thermopile. They were constructed with extreme care so as to ensure the least possible inherent potential. When tested at 23° and at 100° a potential of 0.8 microvolt was developed which amounted to 200 microvolts per degree

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[1] J. W. Williams and F. Daniels, THIS JOURNAL, **46**, 904 (1914).

[2] G. F. Davies, M.Sc. Thesis, University of British Columbia, 1939.

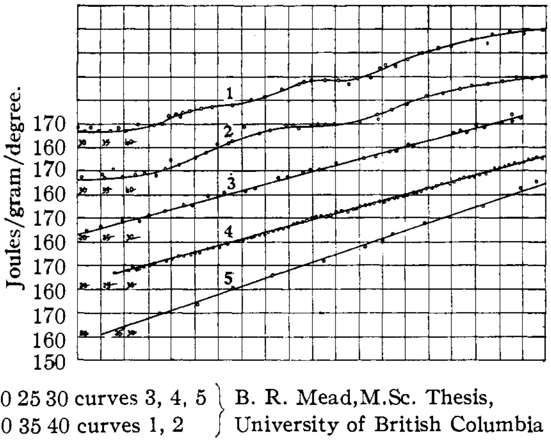
[3] W. P. White, "The Modern Calorimeter," The Chemical Catalog Co., New York, N. Y., 1928.

corresponding to a temperature difference of 0.005°. The thermels were consequently considered to be accurate enough for the proposed measurements.

The resistance thermometer, the resistor and the Eppley cell had all been previously standardized by the U. S. National Bureau of Standards. The resistor and cell values were expressed in terms of international units. Hence the joule is likewise expressed as the international joule, throughout this paper. The calorie was taken as the equivalent of 4.183 international joules. Using Burlew's[4] value for the specific heat of toluene, the water equivalent was found to be 38.0 joules at 30° with an estimated increase of 0.1 joule for each 10° rise in temperature. The apparatus was so constructed that either manual or photoelectrical control could be used to equalize the temperatures of the liquids in the outer and inner baths. The only advantage realized by the latter method over that of the former was the possibility of making more measurements at any one time and that only with the *trans* modification.

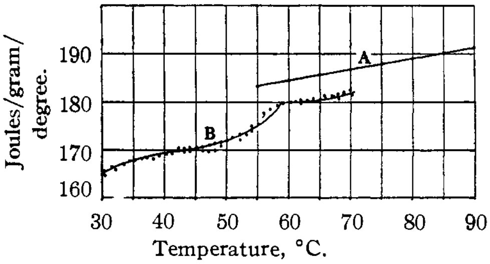
Experimental Results

The experimental results are illustrated in the following series of graphs. It is at once evident from Graph I that there is qualitatively a difference of behavior between the *cis*- and *trans*-decalin, particularly in the temperature region of 50–60°. Lines (1) and (2) illustrate the results obtained with repeated runs on the same sample and on different samples of the *cis* form, while that of (3) and (4) illustrate the regular behavior of the *trans* form. In case (4) photoelectric control was utilized, but it should be stated that this method of control between the temperatures of the inner and outer cups when dealing with the *cis* isomer, was unsuccessful. Line (5) shows the behavior of the calorimeter with respect to a sample of xylene.



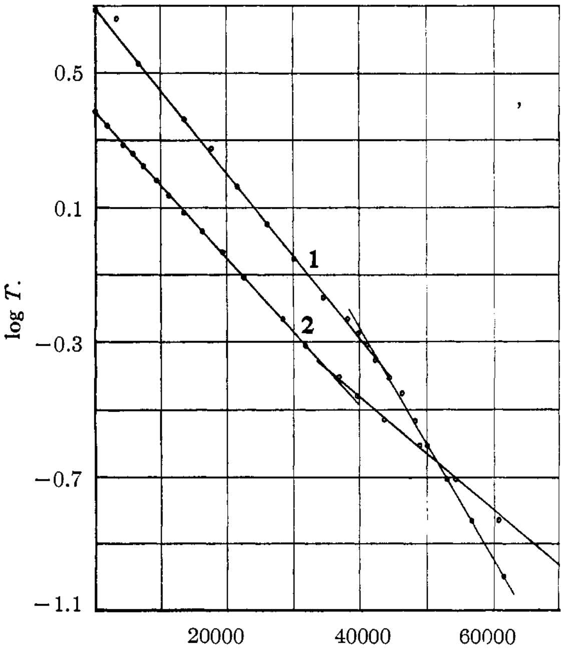
Graph I.—Specific heat of *cis*- and *trans*-decahydronaphthalene from 20 to 120° in j./g./°C.: lines 1 and 2, typical performance of calorimeter with various samples of the *cis* isomer; line 3, results for the *trans* isomer with manual control; 4, with photoelectric control; line 5, results for a sample of xylene; heating rate in all cases, 0.9 watt.

In the course of measurements of various physical properties of the *cis*-decalin, there were indications that some sort of transformation occurred in the temperature region of from 50–60°. Hence two other lines of attack on this problem were pursued, the first consisted in lowering the heating rates from 0.9 to 0.3 watt; the second in using the former heating rate but starting with an initial temperature of 55° instead of 25° or 30°. The results of the first method are shown in line B of Graph II.[6] The second method gave the interesting information that the behavior of the *cis* isomer was as regular as that of the *trans* isomer if the starting temperature was set at 55° (line A).[6]



Graph II.—Specific heat of *cis*-decahydronaphthalene. Performance of calorimeter: A, with *cis* isomer initial temperature 55°, heating rate 0.9 watt; B, two runs with *cis* isomer, heating rate 0.3 watt.

This irregular behavior of the *cis* isomer in contrast to that of the *trans* isomer led to a series of measurements on the heating and cooling rates of the first mentioned isomer. For this purpose the calorimeter was found convenient. No change in set-up was required beyond that of disconnecting the thermopile leads to the potentiometer and connecting them directly to the galvanometer. This had previously been calibrated by noting the galvanometer deflections from known temperature differences between the outside bath and the inner cup containing the decalin. A sample set of heating and cooling curves is shown in Graph V. Here log Δt was plotted against the time in seconds. The weight of sample was 151.28 g. and the outside bath temperature for the heating curve was held at 51.63° and for the cooling curve 48.765°. In all cases the initial temperatures of the material in the cup were about 5° higher or lower than the outside bath temperature depending upon what type of curve was desired. Three different samples were measured several times by two independent operators (McLellan and Robinson). The intersections all fell between 50.2 and 50.4° (Graph III). A sample of *cis*-decalin containing not more than 5% of the transform gave no discontinuity in the log Δt time plot.



Graph III.—Heating and cooling curves of *cis*-decalin: 1, heating, transition point 50.4°; 2, cooling, transition point 50.29°.

The results definitely suggested a transition point in the liquid phase. Attention was therefore directed toward a determination of the heat of transition. It was apparent that the adiabatic method would yield no satisfactory values. Hence efforts were directed toward the non-

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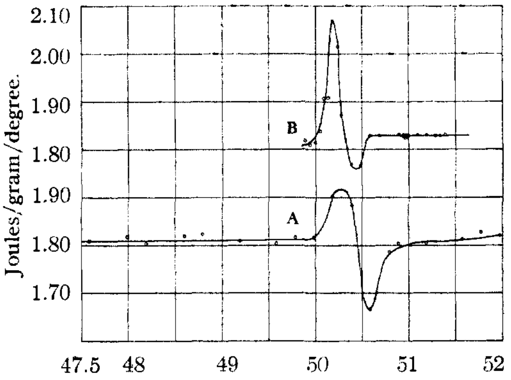
[4] J. G. Burlew, THIS JOURNAL, **62**, 696 (1940).

[5] Donald Ellis McLellan, M.Sc. Thesis, University of British Columbia, 1943.

[6] Harold Morton Graham, M.Sc. Thesis, University of British Columbia, 1944.

adiabatic method which, as had been pointed out by White,[2] could be made equally reliable. This required little change in the calorimetric set-up since the galvanometer deflections had previously been determined for temperature differences between the outside bath and the inner cup liquid. The operations were conducted as follows: the outside bath temperature was set initially at approximately 47° and held constant to within ±0.05°. Equilibrium between the inner and outer temperatures was attained well within one hour. A definite amount of heat was then added and the rise in temperature noted by the amount of galvanometer deflections at regular time intervals. The temperature of the outside bath was then raised slightly and the performance repeated.

It was extremely difficult to estimate the quantity of heat required to ensure a measurable temperature rise in temperature intervals from 50–51° because of the irregular behavior of the hydrocarbon. The figures (A) and (B) in Graph IV represent the limiting values of a region in which all the other values obtained for different runs fell.[7]



Graph IV.—Specific heat of *cis*-decalin method.

Discussion of Results

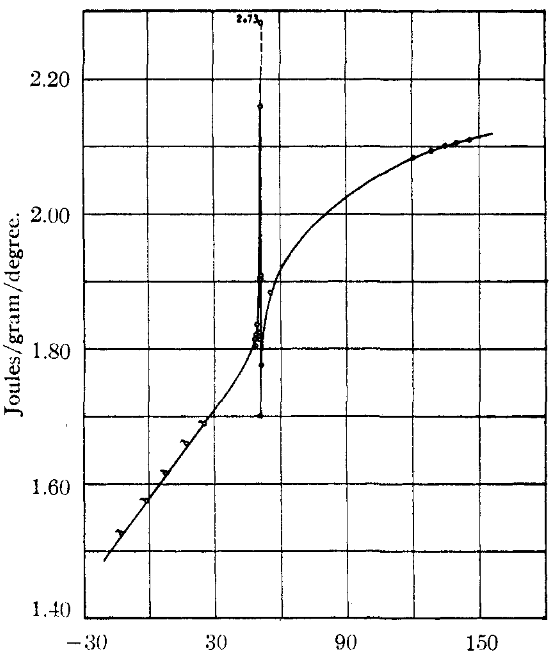
The preceding graphs illustrated that consistent values of the specific heat for the *trans* form could be obtained but not so for the *cis* modification, nevertheless it was thought convenient to plot the results for both of the forms on a large scale graph. From the smooth curve values of the specific heats from 20–140° for the *trans*-decalin and from 20–70° for the *cis*-decalin have been read off for ten degree intervals and recorded in Table I.

TABLE I

SPECIFIC HEATS IN CALORIES PER GRAM—DECAHYDRONAPHTHALENES

T, °C.	*trans*	*cis*	*T*, °C.	*trans*
20	0.3866	0.3989	80	0.4645
30	.3977	.4085	90	.4745
40	.4104	.4207	100	.4865
50	.4237	.4317	110	.4986
60	.4363	.4470	120	.5106
70	.4483	.4573	130	.5220
			140	.5336

At our request Parks and Hatton[8] measured the specific heats of the *cis*- and *trans*-decahydronaphthalene from 80 to 298.16°K. Their value for the *trans* form at 298.16°K. is given as 0.3997 whereas our value at that temperature is 0.3922. In the case of the *cis* isomer the value taken from the smooth curve for the same temperature is 0.3955, a value considerably lower than that recorded by the above-mentioned authors, *viz.*, 0.4041. It was further found that the slope of the averaged *cis* line is lower than that of the *trans* line and that the two lines intersect at about 50°. The reason for this will be discussed later. Next a curve based on the values obtained by Parks and Hatton,[8] Robinson,[7] and Graham[6] for the *cis* compound was constructed as shown in Graph V.



Graph V.—Specific heat of *cis*-decahydronaphthalene; ȯ, after Parks and Hatton.

It is apparent from the nature of this curve that we are here confronted with a second order phase change in the liquid state or in other words *cis*-decahydronaphthalene shows a λ-region lying between 50.1 and 50.5°. Evidence for an intermolecular or intramolecular change at this temperature was encountered in the course of several other physical measurements made on these two hydrocarbons. Thus the surface tension–temperature measurements indicated some form of discontinuity at about 50° for the *cis* but not for the *trans* compound.[9] Numerous attempts to discover a discontinuity in the refractive index temperature relationships were inconclusive except within the temperature interval from 50–51°. Here no definite boundary for the critical angle could be observed when using a Pulfrich refractometer owing to the turbidity of the liquid *cis* compound. A change in structure, it was reasoned, should be reflected in the vapor pressure–temperature curves but again these were found to be inclusive even though several hundred measurements were made on highly purified samples by different observers. Excellent agreements were obtained for the vapor pressures between 50° and 110° but none whatever below 50°. Density and viscosity measurements yielded no information as to structural changes for the *cis* isomer at the temperature in question.

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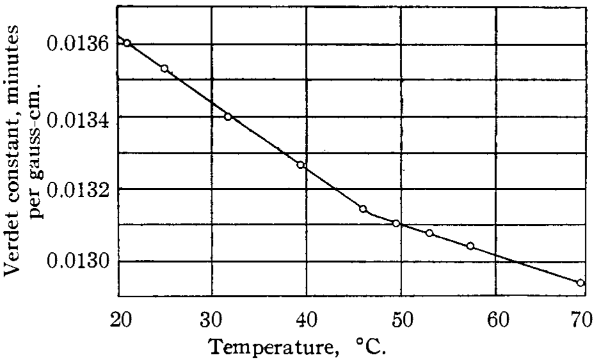
(7) Marian Robinson, M.A. Thesis, University of British Columbia, 1945.

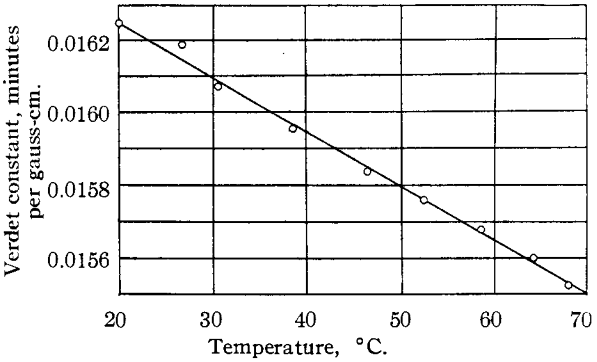
(8) G. S. Parks and J. A. Hatton, THIS JOURNAL, **71**, 2173 (1949).

(9) W. F. Seyer and C. H. Davenport, *ibid.*, **63**, 1585 (1941).

As shown by Graph III, the heating and cooling rate measurements gave quite positive indications of some form of structural change within the temperature interval of 50.1 to 50.5. However, in order to secure more supporting evidence for this type of change the senior author requested Professor H. D. Smith and his assistants in the Physics Department of the University of British Columbia to investigate both the change in the Verdet constant and the Raman spectra with temperature for the two isomers of decahydronaphthalene.[10] Their results are to be published shortly but permission has been granted to present the data in the form of Graphs VI and VII. A discontinuity in the linear relationships between the Verdet constant and temperature appears without question although the intersection of the two lines is somewhat below the transition region as found by other measurements. Professor G. Glockler[11] of the State University of Iowa, to whom we sent samples some years ago with a request that he investigate the Raman effect of the two hydrocarbons, has allowed me to quote this statement of his: "We studied the light scattering of these two isomers at 25° and 70° and found that *trans*-decalin shows the same light scattering intensity over this temperature range. On the other hand, *cis*-decalin scatters much more strongly at 25° than at 70°. It seems therefore that *cis*-decalin does show a different behavior than does *trans*-decalin insofar as light scattering is concerned." Davies and Gilbert[12] have reported the heat of isomerization, $-\Delta H$, *cis*-(liquid)-*trans*-(liquid) to be 2.12 kcal./mole. Hence, since the *trans* form is more stable at low temperatures than the *cis* form isomerization during measurements could conceivably take place and thereby affect the results. It has been shown that the velocity of transformation at 45° is very high in the presence of anhydrous aluminum chloride.[13] However, tests carried out on both samples of the *cis* and *trans* form indicated no change in f.p. for at least one year if sealed in tubes under their own vapors and kept at room temperatures. This was not so at temperatures of 70° and above in the presence of air as found by Davenport.[14] His work showed conclusively the production of unsaturated compounds upon heating either isomer in air, but the amount of unsaturation as measured by increase in iodine number was considerably greater for the *cis* than for the *trans* isomer. It should also be pointed out that experience has shown decalin to be dehydrogenated during prolonged fraction at low pressures. Heating samples of both compounds in sealed glass tubes for 20 hr. at 170° and for 6 hr. at 200° produced no observable amount of unsaturation but did show a slight change in density for the *cis* compound. Results on the change of density of the *cis* form were not consistent. One would expect under these conditions some isomerization to the *trans* isomer and a decrease in density but instead an increase was observed. The explanation advanced is that transformation into a third isomer occurs as already suggested by Zelinsky and Turova-Pollak.[15]



Graph VI.—*cis*-Decahydronaphthalene.



Graph VII.—*trans*-Decahydronapthalene.

While experience indicated that the rate of conversion of the *cis* to the *trans* isomer was low in glass tubes it was realized the case might be quite different in the presence of the copper, brass and nichrome wire of the calorimeter parts which could act as catalytic agents. It was therefore thought possible that the heat of isomerization could become great enough to influence the specific heat measurements. Evidence that such is the case was obtained in two ways. In determining the heating and cooling curves it was found that after the same sample had been used more than three times, the difference of the slopes of the two plotted log Δt time lines appeared to become less. In fact, after the fifth time this difference in slope was barely detectable. Also whenever a sample of the *cis* compound had been used in the specific heat measurements and a temperature of 110° exceeded, the freezing point of the material was lowered. Partial conversion of the *cis* to the *trans* form would explain the fact that the average specific heat curve of the *cis* isomer gave specific heat values below that of the *trans* isomer above 90°. Even in the case of Graham's[6] determination the slope of the specific heat temperature curve is too low probably because a lower rate of heat input required a much longer period of time than those of earlier runs with a considerable amount of heat liberation because of isomerization.

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(10) H. D. Smith, private communication, Nova Scotia Research Foundation.

(11) G. Glockler, private communication, Department of Chemistry and Chemical Engineering, State University of Iowa.

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

(13) W. H. Seyer and C. W. Yip, *Ind. Eng. Chem.*, **41**, 378 (1949).

(14) Charles H. Davenport, M.Sc. Thesis 1939, University of British Columbia.

(15) N. D. Zelinsky and M. B. Turova-Pollak, *Ber.*, **58B**, 1292 (1925).

In order to obtain some information as to the amount of conversion in the calorimeter the freezing point of the material in the cup was determined after three separate runs where the maximum temperature did not exceed 53°. No change was found although the time during which the material was above room temperature was about 10 hr. The difficulty in obtaining consistent values of the heat content of the *cis* hydrocarbon in the transition region can be realized when it is borne in mind that two rate processes are involved; *viz.*, the conversion of the A *cis* form to the B form, and the conversion of the *cis* to the *trans* isomer.

Attention should be drawn to the rather puzzling results recorded in figures A and B of Graph V. In making complete runs through the transition region it was noticed that the specific heat values fell far below the normal immediately after the crest was reached and approached the normal value only after further increments of heat had been added. A phenomenon similar to this was observed by Giauque and Wiebe[16] when measuring the heat capacity of hydrogen iodide in the transition region about 125°K. They showed the difficulty of attaining equilibrium in some of these second order phase transitions where considerable amounts of energy are absorbed over small temperature ranges. One might hazard an explanation for this behavior similar to that suggested by the abovementioned authors for hydrogen iodide.

The reversible nature of the reaction was well established by the heating and cooling experiments and also by the surface tension measurements. From these it was further possible to gain some idea of the order of the velocity of the conversion process. Experience established that in the neighborhood of 50° a time interval of at least 20 minutes was required for the difference in height between the two liquid levels in the tubes to reach a steady state. The difference in differential height at 60° between what was found and expected was 0.01 cm. Since the cathetometer could be read to 0.001 cm. there was never any doubt as to this value. Lowering the temperature to 50° and holding it at this point for 20 minutes restored the differential height to its initial value. This of course does not imply that complete conversion had taken place because of the limited sensitivities of the surface tension measurements.

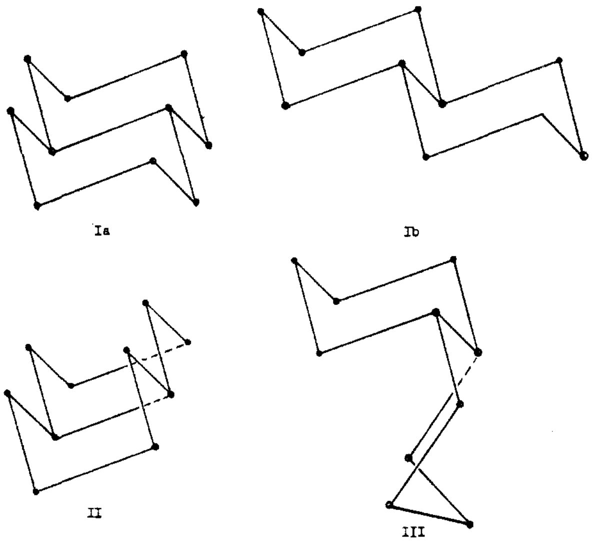

Fig. 1.—After Barton[20]: Ia and Ib, *trans* after Barton; II, *cis*, Mohr form; III, *cis*, Bastiansen and Hessel.

The tentative nature of the specific heat measurements does not allow a quantitative estimation of the heat of transformation of form A into B. However some idea as to the approximate value appeared to us to be desirable so a curve was constructed from the points recorded in curves A and B of Graph V. From an estimated area of the hump a value of 2.23 cal. per mole was obtained. This is an extremely small quantity, consequently the entropy of transitions must be a very small quantity.

A satisfactory explanation as to the molecular nature of the change involved in the temperature interval of 50.1 to 50.5 is difficult to make on the basis of the data available at present. However some speculation as to the nature of the change might be in order. The isomers of decalin are completely saturated, hence association in the normal sense can be excluded. Further the heat of transformation is so small over this temperature interval that the isomerization mechanism *cis–trans* which involves a rupture of the bond could hardly be significant. Both Sachse[17] and Mohr[18] had postulated the existence of two stable geometrical isomers for the cycloparaffins but it remained for Wightman[19] to demonstrate by means of models that other spacial forms could exist. There are four possible forms for the *cis* isomer and three for the *trans*. The form F can be rotated without strain in the bond angle to models A, C and D. The *trans* models G and E are interconvertible without strain, but B cannot be converted into either E or G. Wightman's F corresponds to Mohr's original form and is represented by No. II (Fig. 1) taken from Barton's[20] illustration. No. III of this figure represents the form of *cis*-decalin in the vapor state as put forward by Bastionsen and Hassel[21] as a result of electron diffraction measurements. It approximates in form to A, C and D of Wightman's models. Hence the postulate is advanced that the stable configuration of the *cis*-decalin molecule below 50.10 is that of Wightman's F or its equivalent, Barton's II, and that above this temperature the stable configuration is somewhat like Wightman's A, C or D but with a small amount of strain in the bond angle. Further evidence to support this contention might be found in the behavior of the dielectric constant of *cis*- and *trans*-decalin when passing from the liquid to the solid state.[22] The *cis* isomer behaves normally, *i.e.*, the dielectric constant falls in passing from the liquid to the solid state, but not so for the *trans* isomer, for in this case the dielectric constant

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(16) W. F. Giauque and R. Wiebe, THIS JOURNAL, **51**, 1444 (1929).

(17) H. Sachse, *Ber.*, **23**, 1363 (1891).

(18) E. Mohr, *ibid.*, **55B**, 230 (1922).

(19) W. A. Wightman, *J. Chem. Soc.*, **127**, 1421 (1925).

(20) D. H. R. Barton, *ibid.*, 340 (1948).

(21) O. Bastionsen and O. Hassel, *Nature*, **157**, 765 (1946).

(22) Wm. F. Seyer and Gordon M. Barrow, THIS JOURNAL, **70**, 802 (1948).

rises in going from the liquid to the solid. Further, a discontinuity could be observed both for the *trans*-decalin and cyclohexane during the freezing process. This would suggest some change in structure so as to enable the molecule to adjust itself to the minimum energy state in the crystal lattice. Hence the rigid chain forms of *trans*-cyclohexane and *trans*-decalin (type II of Wightman) must be excluded, in favor of Wightman's B and C for cyclohexane and G or E for *trans*-decahydronaphthalene. Again the value of the dielectric constants of the *cis* and *trans* forms in the solid state appear to be the same as far as experimental results showed. This would indicate the same crystal structure for both and would imply a very close similarity in molecular structure. This can most easily be perceived in Wightman's E and C models. Again, if the excess scattering for the *cis* compound below 50° as observed by Glockler[23] and Tung is due to the formation of cybotactic units then these could most easily arise from Wightman's (F) form.

In conclusion the senior author wishes to express his gratitude for the valuable assistance rendered in the course of this work: *viz.*, George Francis Davies, Donald Ellis McLellan, Marian Robinson, Morton Harold Graham, Stuart Donald Cavers, B. R. Mead and Henry J. Howie; also to Professors Smith and Glockler for their interest in the study of the properties of the two compounds of decahydronaphthalene.

[23] Private communication, Geo. Glockler, University of Iowa.

LOS ANGELES 4, CALIFORNIA

[CONTRIBUTION FROM THE BANTING AND BEST DEPARTMENT OF MEDICAL RESEARCH, UNIVERSITY OF TORONTO]

On the Crystallization, Structure and Infrared Spectra of Saturated L-α-Lecithins

BY ERICH BAER

RECEIVED AUGUST 25, 1952

A procedure of crystallization is described by which it is possible to obtain the L-α-(dimyristoyl)-, L-α-(dipalmitoyl)- and L-α-(distearoyl)-lecithins in a distinctly crystalline state. The elementary composition of the crystalline lecithins is in agreement with formula: $\mathrm{RCOOCH_2\text{–}RCOOCH\text{–}CH_2OPO(O^-H^+)OCH_2\text{–}CH_2N^+(CH_3)_3(OH)^-}$ but not with $\mathrm{RCOOCH_2\text{–}RCOOCH\text{–}CH_2OPO(\underline{O)OCH_2\text{–}CH_2N}(CH_3)_3}$. The infrared spectra of the pure lecithins are reported.

Various investigators[1,2,3] studying the catalytic reduction of naturally occurring lecithins reported that they had obtained the hydrolecithins in a crystalline state. With the exception of Paal and Oehme,[4] who described their material as cubical crystals, no mention was made of the crystal form. More recently, however, Thannhauser, Benotti and Boncoddo[5] reporting the isolation of dipalmitoyllecithin from beef lung stated that they had obtained the phospholipid in aggregates of small needles by recrystallization from either diisobutyl ketone or a mixture of acetone and acetic acid (40:1).

Three years ago the author and M. Kates described the synthesis of the dimyristoyl-, dipalmitoyl- and distearoyl-L-α-lecithins.[6] To obtain these lecithins in a crystalline form they were reprecipitated from warm (60–80°) diisobutyl ketone. Although the material thus obtained gave distinct X-ray diffraction patterns and exhibited birefringence under polarized light, it did not possess a definite crystal form. In addition it was found that the procedure was not as harmless as had been assumed. The three lecithins after recrystallization from diisobutyl ketone proved to be less stable than either the crude products or lecithins which had been obtained by reprecipitation from chloroform with acetone at room temperature.[7]

The recrystallization of the lecithins from warm dioxane, which yields lecithin crystals large enough to be seen at low magnification[6] may also be hazardous because of the relatively high temperature (65–70°) at which the crystallization has to be carried out.

It seemed therefore desirable to find a method of crystallization which would be non-injurious to the lecithins and which would produce these substances in a distinctly crystalline form. This has now been accomplished by using chloroform as solvent and ether as precipitant, and by conducting the crystallization of the lecithins slowly and in dilute solution at or near room temperature. To obtain well-formed crystals it was found important (1) that the precipitant be added in amounts just sufficient to make the solution saturated with regard to the lecithin, but insufficient to cause their immediate precipitation, (2) that with increasing chain length of the fatty acids the crystallization of the lecithins be carried out in increasingly greater volumes of the chloroform–ether mixture, and (3) that the solutions be kept as undisturbed as possible. In one instance in which the crystallization of the L-α-(dimyristoyl)-lecithin was carried out using twice the volume of chloroform and 2.3 times the volume of ether reported in the experimental part for the recrystallization of this substance, a portion of the lecithin was deposited on the walls of the test tube in the form of rosettes composed of long and narrow prisms which measured up to 5 mm. in length.

In 1926, Grün and Limpächer[8] reported a synthesis of DL-α-(distearoyl)-lecithin. The analysis

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