

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF BRITISH COLUMBIA]

The Vapor Pressures of *cis*- and *trans*-DecahydronaphthaleneBY WM. F. SEYER AND CLARENCE W. MANN¹

This investigation was carried out to supplement information which has been collected in these laboratories on the physical and chemical properties of the *cis* and *trans* isomers of decahydronaphthalene.

Materials.—The isomers of decahydronaphthalene were obtained by rectification of crude hydrogenated naphthalene at a pressure of 9 mm. absolute, in a column with Stedman-type packing. Subsequent to the rectification, the isomers were further purified by recrystallization to a constant freezing point as described by Seyer and Walker. The freezing points were: -43.26° and -30.68° for the *cis* and *trans* isomers, respectively.

Apparatus and Procedure.—The apparatus used was of the conventional type, modified so as to permit the measurements to be made over a large range with the same sample of hydrocarbon. In one respect it consisted of two manometers in series, one of which could be completely immersed in a bath not over 50 cm. in height. Special precautions were taken to ensure thorough removal of air from the samples. Thus, each hydrocarbon was evaporated and condensed successively into three flasks under vacuum before being collected in the reservoir bulb of the apparatus. The bath liquids used were methyl alcohol, water and petrolatum oil, respectively, as the temperature was raised. All temperatures were measured by a calibrated platinum resistance thermometer. During the time of readings, which lasted from one to several hours, temperatures did not vary more than 0.08° . The differential heights of the mercury were read by means of a cathetometer and a specially prepared calibrated scale. All differential readings were corrected to 20° .

The readings for both isomers are recorded in Table I.

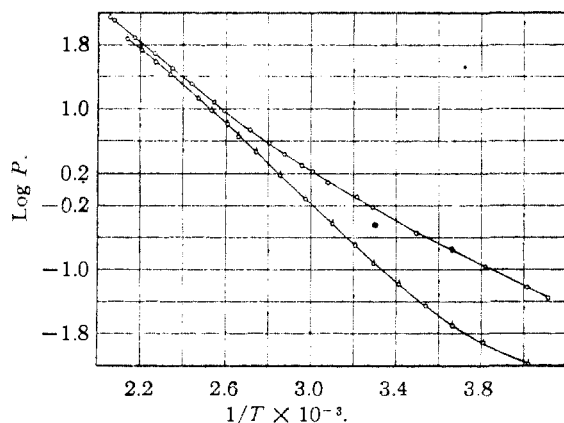


Fig. 1.—○, *trans*-Decahydronaphthalene; △, *cis* form.

Discussion of Results

The vapor pressure curves, obtained when the pressures were plotted against temperature on a large scale graph, indicated the b. ps. of the *cis* and *trans* isomers to be 194.5° and 185.8° , respectively. These values are in close agreement with those found previously by a standard boiling point determination method, *viz.*, 194.6° and 185.5° .²

(1) Holder of the Standard Oil of B.C. Fellowship for 1943-1944.

(2) Seyer and Walker, *THIS JOURNAL*, **60**, 2125 (1938).

TABLE I

Temperature, °C.	Pressure, cm. of Hg at 20°	Temperature, °C.	Pressure, cm. of Hg at 20°
<i>trans</i> isomer		<i>cis</i> isomer	
-30.0	0.044	-29.5	0.038
-24.1	0.060	-19.2	0.065
-11.1	0.107	-10.0	0.086
-0.7	0.173	0.0	0.109
0.0	0.182	12.0	0.148
13.0	0.287	20.0	0.182
30.9	0.603	38.0	0.344
38.9	0.823	43.4	0.400
51.5	1.202	49.9	0.530
59.7	1.672	50.4	0.541
65.3	2.000	52.9	0.606
74.4	2.702	56.9	0.731
83.5	3.818	60.0	0.824
95.5	5.501	70.0	1.257
112.4	9.511	80.1	1.950
119.4	12.110	92.4	3.281
136.7	20.685	105.1	5.450
152.3	32.065	109.8	6.315
168.0	48.949	112.4	6.866
187.1	77.605	124.6	10.521
208.8	128.02	148.7	22.582
212.9	139.64	172.7	43.428
223.4	172.23	194.7	76.102
235.3	214.53		

In Fig. 1 plots of $\log p$ against $1/T \times 10^{-3}$ are shown. It shows the liquids to behave somewhat abnormally with respect to temperature changes. The curves are approximately linear only at the upper temperatures. Since the pressures were reproducible either with ascending or descending temperatures and as the apparatus was frequently checked by repeatedly taking readings at 20° and 0° , we feel the accuracy over the range covered should be within 0.5%.

The equation $\ln p = A/T + B \ln T + C$ was found to fit the curves reasonably well when the constants obtained by the method of least squares were used.

TABLE II

	A	B	C
<i>cis</i>	-1702.20	6.8139	-34.32
<i>trans</i>	-2182.38	6.8509	-32.64

The differences between the measured and calculated values were less than 0.5%, which is about the limit of accuracy of measurement as stated before.

Critical temperatures were calculated by the method suggested by Hougen and Watson.³ This gave the values 417.5° and 398.2° for the *cis* and *trans* forms, respectively. Davenport calculated

(3) Hougen and Watson, "Industrial Chemical Calculations," John Wiley and Sons, Inc., New York, N. Y., 1936.

the values to be 428.6 and 409.5° from surface tension measurements.⁴

The molal latent heats at the b. p. were calculated as well as the Trouton constant by the use of the Clausius-Clapeyron equation and by an equation suggested by Kistyakowsky.⁵ The values are given in Table II, the values under 1 being those obtained from the former and those under 2 from the latter equation.

TABLE III

	Molal latent heats		Trouton constant	
	1	2	1	2
<i>trans</i>	9960	9614.9	21.7	20.9
<i>cis</i>	10210	9799.4	21.8	20.9

(4) C. H. Davenport, M.A.Sc. Thesis, University of British Columbia, 1939.

(5) Kistyakowsky, *Z. physik. Chem.*, **107**, 65 (1923).

It is obvious from Fig. 1 that the latent heat is a linear function of the temperature only over a small range of temperature.

In conclusion, we wish to express our gratitude to the following for their assistance in this work: T. Pilkington, I. Rush, J. Leslie and H. Nemetz.

Summary

1. The vapor pressures of *cis*- and *trans*-decahydronaphthalene have been measured over a range of temperature from -30 to 223°.

2. The critical temperatures, latent heats and Trouton constant have been calculated from the data.

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Kinetics in Acid Media: The Correlation of Reaction Rates with Acidity Function

BY CHARLES W. DEANE

Recently, Lewis and Bigeleisen¹ presented an extension of available acidity function data into fuming sulfuric acid concentrations by a plot showing the effect of sulfur trioxide up to 100% sulfur trioxide concentration. Since Hammett and Deyrup² were able to correlate rates and acidity function up to 100% sulfuric acid, a test of the new data with related kinetic data is in order, and the quantitative results and interpretation of such a study for five organic acid decompositions are here presented.

Through assuming coincidence at 50 mole % sulfur trioxide with earlier results² upon sulfuric acid for concentrations up to 100% sulfuric acid, the acidity function has been presented by Lewis and Bigeleisen as a direct extension of the data of Hammett and Deyrup because the results of the latter are said¹ to be "more precise." Simultaneously to the publication of Lewis and Bigeleisen,¹ new kinetic data obtained in fuming sulfuric acid were presented and discussed,³ and the variant effects of sulfur trioxide on organic acid decompositions in oleum published to date were given. A summary of these effects is here shown:

Organic acid	Influence of SO ₃ on reaction rate
Oxalic ⁴	Slight (increase to approx. 14% SO ₃ ; decrease above)
Malic ⁵	Marked inhibition
Citric ⁶	Pronounced inhibition
Formic ⁷	Acceleration (degree not measured)
<i>o</i> -Benzoylbenzoic ³	Moderate acceleration

(1) Lewis and Bigeleisen, *THIS JOURNAL* **65**, 1144 (1943).

(2) Hammett and Deyrup, *ibid.*, **54**, 2721 (1932).

(3) Deane with Huffman, *Ind. Eng. Chem.*, **35**, 684 (1943).

(4) Wiig, *THIS JOURNAL*, **52**, 4737 (1930).

(5) Diltmar, *ibid.*, **52**, 2746 (1930); Whitford, *ibid.*, **47**, 953 (1925).

(6) Wiig, *ibid.*, **52**, 4720 (1930).

(7) Deright, private communication.

It was pointed out³ that since organic oxygen compounds are highly ionized basically in strong sulfuric acid, acid-base catalysis is effective; because of the exceptional behavior of oxalic, malic, and citric acids, the reactions for these acids appear anomalous, and to be governed only incidentally by simple ionic factors.

To explain fully the reaction mechanism, an all-inclusive theory should cover all of these various phenomena. A mechanism should correlate known facts and predict new ones. Aimed to this end, Hammett and Deyrup² have developed a correlation showing a reasonable constancy in the sum of log *k* (reaction velocity constant) plus *H*₀ (acidity function) for the decompositions of six organic acids, and for acetophenone oxime, in sulfuric acid concentrations up to 100%.

The correlation of the velocity constants in the decomposition of *o*-benzoylbenzoic acid with the extension of the acidity function by Lewis and Bigeleisen is quite striking. Table I shows the constancy of the sum of *H*₀ and log *k* at various acid and oleum concentrations up to 28.8% sulfur trioxide concentration. Part of this table supersedes part A of Table IV of Hammett and Deyrup² which is based on an erroneous earlier plot of Gleason and Dougherty⁸ wherein the sulfuric acid axis is 10% low throughout.

Owing to the widely variant behavior in fuming acid indicated in the introduction, certain questions concerning correlation above 100% sulfuric acid arise: (1) whether *o*-benzoylbenzoic acid, as previously suggested,³ is more ideal when the earlier correlation method² is applied? (2) Would data on some other studied organic acid serve better?

To test these points, calculations with the new data of Lewis and Bigeleisen have been made, to-

(8) Gleason and Dougherty, *THIS JOURNAL*, **51**, 310 (1929).