$$\Delta F\ 13200 - 33.6T \text{ cal./mole}$$
$$\Delta H = 13200 \text{ cal./mole}$$
$$\Delta S = 33.6 \text{ cal./mole-deg.}$$

During these observations it is believed that the temperature measurements were in error by no more than 0.2° K. The sickle gage employed possessed sufficient sensitivity so that a pressure differential of 0.5 mm. could be readily detected. The mercury manometer was observed to the nearest 0.1 mm. by the use of a cathetometer.

Discussion

The reaction for which the thermodynamic quantities have been measured is the removal of a molecule of water from a molecule of 1,10-phenanthroline monohydrate, two hydrogen bonds being broken in the process. Accordingly values of 14.5, 13.0 and 13.2 cal./mole were obtained for ΔH of the hydrates of 1,10-phenanthroline, the 5-bromo and the 5-methyl derivatives, respectively. Since the nitrogen atoms in 1,10-phenanthroline are equivalent, the value of $\Delta H/2$, 7.25 cal./mole, may be considered as representing the strength of one hydrogen bond.[10] The presence of a substituent in the 5 position would be expected to affect the electron density around the two ring nitrogen atoms unequally. Therefore, it cannot be assumed that $\Delta H/2$ in these cases represents the strength of a single hydrogen bond but that it is rather the arithmetic average of the two unequal hydrogen bonds.

Compared to the O—H...O bonds measured by other workers,[5,6,7] the O—H...N bonds measured in the present work are quite strong.

It was desired to study further the effect of substituents on the strengths of the hydrogen bonds by measuring the dissociation pressures of some symmetrically 1,10-phenanthrolines. Upon searching for compounds of this class only the 5,6-dimethyl derivative was available, but contrary to expectations no hydrate could be obtained. Perhaps this is due to the extraordinarily high melting point of this compound (272° compared to 114° for the anhydrous 5-methyl compound and 117° for anhydrous 1,10-phenanthroline).

Acknowledgment.—The authors wish to thank the G. Frederick Smith Chemical Co. for the loan of the 1,10-phenanthroline chemicals, and Mr. Paul Anders who fabricated the glass apparatus employed in this investigation.

Summary

1. The dissociation pressures at various temperatures for several 1,10-phenanthroline monohydrates have been measured. From the data the thermodynamic quantities K, ΔF, ΔH and ΔS have been evaluated.

2. The value of the hydrogen bond in 1,10-phenanthroline monohydrate was found to be 7.15 cal./g. mole.

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[10] It is necessary to consider the error introduced by the possible change of the crystal energies of the solid phases due to the removal of the water molecule. According to Wenner (Wenner, "Thermochemical Calculations," McGraw-Hill Book Company, Inc., New York, N. Y., 1941, pp. 23–25) the following empirical rule is followed by organic compounds:

$$\Delta H_f/T_m = 9 \text{ to } 11$$

Where ΔH_f is the molar heat of fusion in calories and T_m the absolute temperature of the melting point. Choosing an average value of 10 for the constant we estimate ΔH_f for 1,10-phenanthroline monohydrate at 3730 cal./g. mole and for the anhydrous material at 3900 calories/g. mole. The value of ΔH_f is 200 cal./g. mole or *ca.* 100 cal./g. mole per bond. When this small correction is applied the value for each hydrogen bond becomes 7.15 cal./mole.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Infrared Absorption Spectra of Some Cyclopropane and Cyclobutane Hydrocarbons

BY JOHN M. DERFER, EDWARD E. PICKETT[1] AND CECIL E. BOORD

The infrared absorption spectra of cyclopropane and cyclobutane have been determined many times and detailed theoretical analyses of these spectra have been carried out.[2]

To date the infrared spectra of only four alkyl-substituted cyclopropanes have been described in the literature. Lankelma[3] and co-workers have published the spectra of 1,1,2-trimethyl- and 1,2-dimethyl-3-ethylcyclopropane. The spectra of methyl-[4] and 1,1-dimethylcyclopropane[5] also have been published recently; a tentative assignment of frequencies was presented for the latter. A theoretical analysis of the infrared absorption spectra of 1-methylcyclobutene and methylenecyclobutane has also been carried out[5]; no spectra of other hydrocarbons of the cyclobutane series have been described.

The paucity of published spectra of substituted cyclopropanes and cyclobutanes is due chiefly to the fact that hydrocarbons of these types are relatively rare and have seldom been synthesized in quantities sufficient to allow a high degree of

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[1] Present address: Department of Agricultural Chemistry, University of Missouri, Columbia, Missouri.

[2] (a) King, THIS JOURNAL, **58**, 1580 (1936); (b) Linnett, *J. Chem. Phys.*, **6**, 692 (1938); (c) Saksena, *Proc. Ind. Acad. Sci.*, **10A**, 449 (1939); (d) Wilson, *J. Chem. Phys.*, **11**, 369 (1943); (e) see also Bonner, *ibid.*, **5**, 704 (1937); Eyster, *ibid.*, **6**, 576 (1938).

[3] Bartleson, Burk and Lankelma, THIS JOURNAL, **68**, 2513 (1946).

[4] Condon and Smith, *ibid.*, **69**, 965 (1947).

[5] Cleveland, Murray and Gallaway, *J. Chem. Phys.*, **15**, 742 (1947).

purification. Reliable infrared spectra of such compounds would be an invaluable aid to workers in this field, since even small quantities of an impure hydrocarbon might then suffice for identification.

The present paper presents infrared absorption spectra of fourteen individual cyclopropane hydrocarbons and seven individual cyclobutane hydrocarbons; the experimental samples, with two exceptions, were available in amounts which permitted obtaining materials of a high degree of purity. These spectrograms not only characterize the compounds for which they were determined, but may be of use in distinguishing between a 3- and 4-membered ring when the presence of one or the other is reasonably expected. No detailed theoretical analysis of any of these spectra has been attempted.

Experimental

Instrumentation.—The infrared spectra were obtained by means of the Beckman IR-2 spectrophotometer. This instrument, thermostated at 25 ± 1°, was calibrated to within 0.03 μ by means of the spectra of water, carbon dioxide and ammonia. The transmissions of the sample and sample cell were measured directly, without comparison with an empty cell, for the purposes of the present qualitative study. The spectra represent a combination of the data obtained from recorder tracings and from point-by-point per cent. transmission measurements. It was not convenient to determine the spectra of all of the samples in the same physical state because of the wide differences in their boiling points.

Samples.—Samples numbered 4, 6, 8, 15, 16, 17, 18 and 19 (see Table I) were obtained from materials previously described by two of the present authors.[6] Numbers 1, 2 and 3 were prepared by Ross Van Volkenburgh[7]; Numbers 5 and 9 by R. W. Shortridge[8]; Numbers 7, 10, 11, 12, 13 and 14 by R. G. Kelso; Numbers 20 and 21 by R. C. Krug. Thanks are due to the laboratories of the National Advisory Committee for Aeronautics which furnished a high-purity sample of methylcyclobutane for checking purposes. Forthcoming publications will give the details of the synthesis of those products whose preparations have not already been reported.[9]

Discussion

Cyclopropane Derivatives.—The spectra of all the cyclopropane derivatives presented in Fig. 1 (Nos. 1 to 14) show a strong absorption band having a peak between 9.8 and 10.0 μ. An absorption band is also prominent in this region in the spectrum of methylcyclopropane recently published.[4] Examination of about 300 spectrograms[10] of hydrocarbons of other types showed that strong absorption bands occur in this region no more often than would be expected on an accidental basis. It appears from our study that this band, centered at about 9.9 μ (1010 cm.$^{-1}$), is characteristic of the cyclopropane ring and that it should prove useful in the qualitative identification of this ring where its presence may reasonably be expected.

TABLE I

SPECTROGRAMS

No.	Hydrocarbon	Estimated minimum purity mole %	State	Cell length, mm.	Pressure, mm.
	Cyclopropanes				
1	Ethyl-	99	Vapor	100	100
2	Isopropyl-	90	Vapor	100	150
3	Isopropenyl-	99	Vapor	100	120
4	1,1-Dimethyl-	97	Vapor	100	140
5	1,1-Diethyl-	99	Liq.	0.09	...
6	1-Methyl-1-ethyl-	99	Vapor	80	250
7	1-Methyl-2-ethyl-[a]	97	Vapor	100	400
8	1-Methyl-1-isopropyl-	97	Liq.	0.025	...
9	1-Ethyl-1-butyl-	97	Liq.	0.09	...
10	1-Methyl-2-*n*-propyl-[a]	97	Liq.	0.025	...
11	1,1,2-Trimethyl-	99	Vapor	100	100
12	1,1,2,2-Tetramethyl-	99	Vapor	100	90
13	1,2,3-Trimethyl-[b]	95	Liq.	0.025	...
14	1,2-Dimethyl-3-ethyl-[c]	90	Liq.	0.025	...
	Cyclobutanes				
15	Methyl-	98	Vapor	100	105
16	Ethyl-	99	Vapor	100	120
17	Ethylidene-	99	Vapor	100	90
18	Isopropyl-	99	Liq.	0.025	...
19	Isopropylidene-	99	Liq.	0.025	...
20	*n*-Butyl-	98	Liq.	0.025	...
21	*n*-Amyl-	97	Liq.	0.025	...

[a] *trans* isomer. [b] *cis-trans-cis* isomer. [c] *cis-cis-cis* isomer.

The spectrum of cyclopropane itself[2a,b,c] shows a prominent band at about 1040 cm.$^{-1}$ (9.61 μ). Linnett[2b] assigned a band at 1051 cm.$^{-1}$ to a mode of vibration in which a methylene group rocks back and forth through the plane of the ring, and another at 1022 cm.$^{-1}$ to a wagging of methylene groups in the plane of the ring. Two ring deformation frequencies were assigned to absorptions at 1187 cm.$^{-1}$ (8.43 μ) and 860 cm.$^{-1}$ (11.63 μ).

It will be noted, however, that the spectra of the various samples of 1,2-dimethyl-3-ethylcyclopropane prepared by Lankelma, *et al.*,[3] as well as our own, Fig. 1 (No. 14) and also our 1,2,3-

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[6] Derfer, Greenlee and Boord, THIS JOURNAL, **71**, 175 (1949).

[7] Van Volkenburgh, Greenlee, Derfer and Boord, *ibid.*, **71**, 173 (1949).

[8] Shortridge, Craig, Greenlee, Derfer and Boord, *ibid.*, **70**, 946 (1948).

[9] In the four cases where geometrical isomerism is possible, the spectrum of only one isomer (that obtained in the highest purity) has been given; since the spectra determined for the other isomers are very similar and less reliable in each case, little would be gained by their inclusion.

[10] "Selected Infrared Absorption Spectrograms." The American Petroleum Institute Research Project 44 at the National Bureau of Standards.

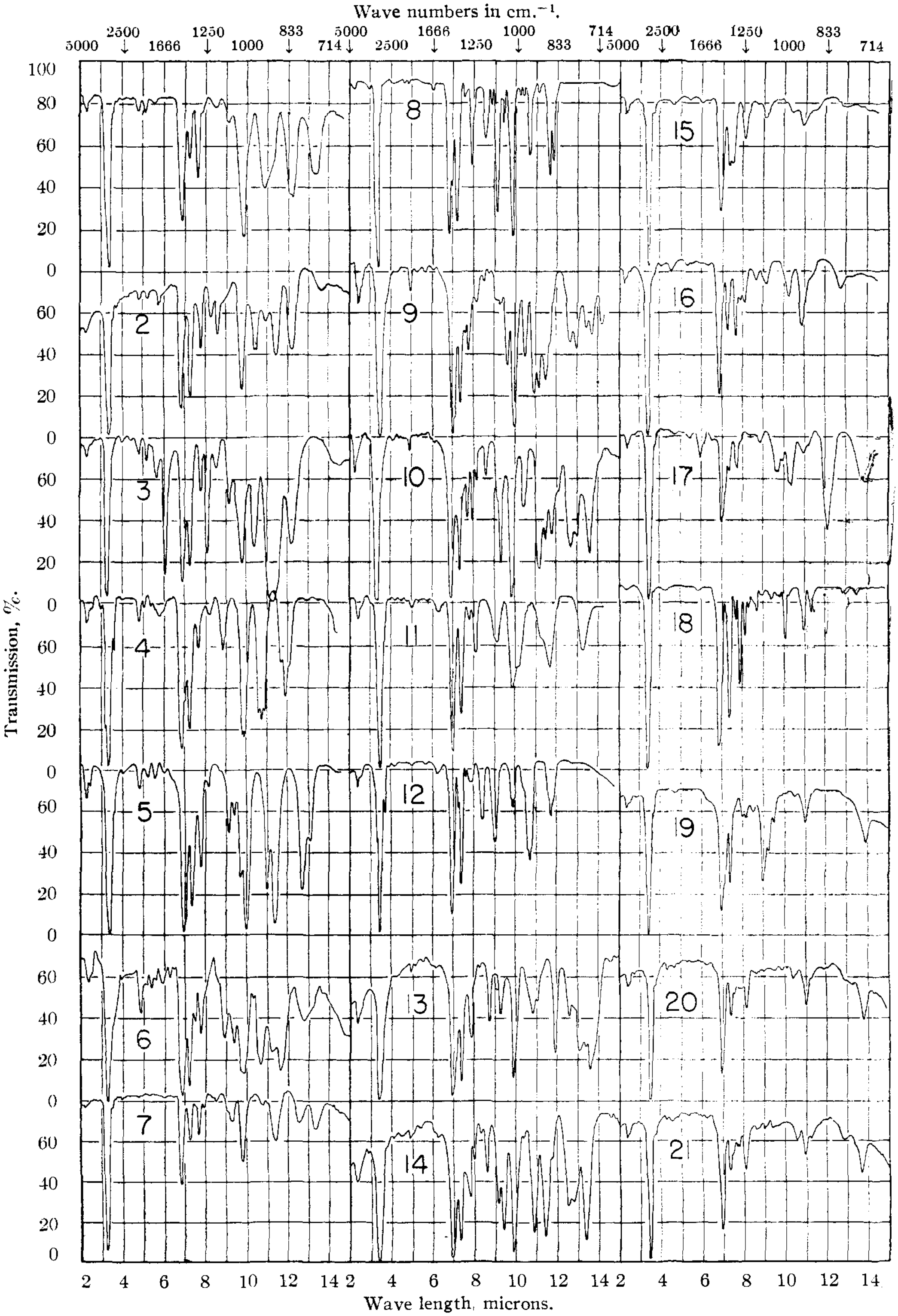

Fig. 1.—Infrared absorption spectra of certain cyclopropane and cyclobutane hydrocarbons (see Table I).

trimethylcyclopropane, Fig. 1 (No. 13), show the 9.9 μ absorption quite strongly although ring methylene groups can be present in them only in impurity molecules. This band therefore appears to be due to a ring deformation. Absorption due to a nearly symmetrical "breathing" ring deformation is probably of low intensity in these compounds, but several unsymmetrical ring deformations are possible in each.

Lankelma and his co-workers[3] use absorptions at 9.75 and 11.55 μ, reported as being typical of cyclopropane itself, for purposes of identifying 1,1,2-trimethylcyclopropane and evaluating its purity. It may be seen from our spectrograms of substituted cyclopropanes that a strong absorption does not occur consistently at 11.6 μ. This wave length region is thus less useful than the 9.9 μ band for purposes of characterization.

Cyclobutane Derivatives.—The spectra of all of the cyclobutanes presented in Fig. 1 (Nos. 15 to 21), show a prominent absorption band peaked at 10.9 to 11.0 μ; this band seems to be characteristic of the cyclobutane ring. In the spectrum of cyclobutane itself, Wilson[2d] found in this region an absorption band which he assigned to two methylene rocking frequencies (903 and 923 cm.$^{-1}$). It remains to be seen whether the band at 10.9 to 11.0 μ will appear with equal regularity in the spectra of cyclobutane molecules having substitution on all of the ring carbon atoms.

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Summary

The infrared absorption spectrograms of fourteen individual cyclopropane hydrocarbons and seven individual cyclobutane hydrocarbons have been determined.

A prominent absorption band peaked at about 9.9 μ has been noted in the spectra of all of the cyclopropanes examined; similarly, a pronounced band peaked at about 11.0 μ has been noted in the spectra of all the cyclobutanes. These bands are suggested as being useful in identifying such ring structures.

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[CONTRIBUTION NO. 712 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution of Aqueous Sodium Bromide and the Standard Heat of Solution of Sodium Bromide at 25°

BY W. E. WALLACE

In the course of a recent study dealing with sodium chloride–sodium bromide solid solutions,[1] a reliable value for the standard heat of solution of sodium bromide was required. After consulting the literature it became evident that the several earlier investigations of the thermal properties of sodium bromide solutions were not sufficiently complete to permit a trustworthy evaluation of its standard heat of solution. The data reported in this paper include a series of measurements of the heats of solution of sodium bromide, and also the heats of dilution of aqueous sodium bromide solutions from saturation (9.192 molal) to 0.002 molal. When these data are combined with the information provided by Hammerschmid and Robinson[2] for extremely dilute sodium bromide solutions, a precise evaluation of the standard heat of solution can be made. In addition, the heat of dilution determinations for concentrated solutions permit a more satisfactory evaluation of the partial molal heat contents at high concentrations than has heretofore been possible.

Experimental.—The calorimeter used in this study has been described.[1] During the solution experiments the calorimeter vessels were provided with devices for crushing the thin glass bulbs used to contain the salt sample to be dissolved. Coincident with the breaking of the bulb containing the sample in one calorimeter vessel, an empty bulb in the other calorimeter vessel was broken to compensate for the very small heat of crushing. Blank experiments (neither side containing a sample) showed that this method for nullifying the heat of crushing was completely effective.

When the calorimeter was used to measure heats of dilution, the crushing devices were replaced with gold-plated brass pipets having volumes of 6.788 and 6.755 ± 0.004 ml. The calorimeter vessels contained 1000 and 1005 ± 1 ml. of water, respectively. The technique employed in measuring heats of dilution has been described in earlier communications from this Laboratory.[3,4]

The sodium bromide employed in this study was

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[1] M. Fineman and W. E. Wallace, THIS JOURNAL, **70**, 4165 (1948).

[2] H. Hammerschmid and A. L. Robinson, *ibid.*, **54**, 3120 (1932).

[3] E. Lange and A. L. Robinson, *Chem. Revs.*, **9**, 89 (1931).

[4] W. E. Wallace and A. L. Robinson, THIS JOURNAL, **63**, 958 (1941).