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TECHNICAL NOTE

No. 1160

THE INFRARED SPECTRA OF SPIROPENTANE METHYLENECYCLOBUTANE AND 2-METHYL-1-BUTENE

By Alden P. Cleaves and Mildred E. Sherrick

Aircraft Engine Research Laboratory
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SUMMARY

The infrared spectra of spiropentane, methylenecyclobutane, and 2-methyl-1-butene were measured in the region from 3 to 14 microns with a rock-salt prism spectrometer of medium dispersion. The pure samples were prepared at the NACA Cleveland laboratory. The vapors of these three C_5 hydrocarbons were investigated at room temperature and at pressures in the range from 80 to 300 millimeters of mercury absolute in a 10-centimeter cell. The spectra were compared with each other and with Raman data for the same compounds.

INTRODUCTION

Spiropentane was prepared at the NACA Cleveland laboratory by the debromination of pentaerythrityl bromide with zinc as described in reference 1. Three hydrocarbon products of this reaction have been studied elsewhere by electron diffraction and identified as spiropentane, methylenecyclobutane, and 2-methyl-1-butene. (See references 2, 3, 4, and 5.) Raman frequencies for these three C_5 hydrocarbons, compiled from the results of several investigators, are listed in reference 2 but their infrared spectra are not available. Apparently the molecule structurally most similar to spiropentane that has been investigated in the infrared is cyclopropane. (See reference 6.) The vibrational levels of cyclopropane based on Raman and infrared data have been reported in reference 7.

Infrared spectra furnish basic data essential for spectrophotometric analysis and for the determination of molecular vibrational levels. This report presents the infrared spectra of samples of spiropentane, methylenecyclobutane, and 2-methyl-1-butene, isolated and purified at the NACA Cleveland laboratory. These spectra of the hydrocarbon vapors were measured at room temperature in the rock-salt region from 3 to 14 microns.

APPARATUS AND MATERIALS

Infrared spectrometers. - Two spectrometers were used in this investigation. One of these spectrometers was adapted to record transmitted infrared radiation as a function of wavelength. This infrared spectrometer, described in detail in reference 8, has a 60° rock-salt prism with faces 6 by 7.5 centimeters, a Globar source, and a thermopile receiver. A high sensitivity galvanometer connected to the thermopile as shown in figure 1 deflects only slightly. A beam of light reflected from the galvanometer mirror so illuminates twin photocells in an amplifier circuit adapted from reference 9 that a Leeds-Northrup pen-recording Speedomax traces the amplified thermopile output. This infrared spectrometer was used for rapid qualitative exploration of the spectra.

The second infrared spectrometer, which is described in reference 10, has a smaller 60° rock-salt prism (faces, 4 by 6 cm), a Nernst glower source, and a thermopile receiver. A micrometer screw attached to the instrument permitted manual adjustment of wave length. Ratios of deflections of a high-sensitivity galvanometer when the infrared beam traversed a 10-centimeter cell, empty and filled with hydrocarbon vapor, respectively, are the percentage transmissions plotted in the spectra.

Hydrocarbons. - The purity of the hydrocarbons prepared and isolated by the Fuels Synthesis Section of the NACA Cleveland laboratory was estimated on the basis of freezing-point data to be high, probably more than 98 percent. The physical properties of the three hydrocarbon samples are reported in reference 1 as follows:

Compound	Freezing point (°C)	Boiling point at 760 mm (°C)	Index of refraction n_D^{20}	Density at 20° C (grams/ml)
Spiropentane	-107.05	39.03	1.41220	0.7551
Methylenecyclobutane	-134.68	42.22	1.42087	.7401
2-Methyl-1-butene	-137.50	31.12	1.37781	.6504

RESULTS

The infrared spectra in the region from 3 to 14 microns for spiropentane, methylenecyclobutane, and 2-methyl-1-butene are presented in figures 2(a), 2(b), and 2(c), respectively. Approximate effective slit widths are indicated. The contours of peaks of the

most intense bands are plotted for two pressures of the hydrocarbons in the cell to verify the position and shape of each peak. The 200-millimeter pressure used for spiropentane was lower than either of the pressures used when determining the complete spectra for the other two compounds; hence, each minimum where transmission is less than 90 percent probably represents an absorption band and some very weak bands may not appear. A survey with the recording spectrometer, however, showed no new bands when the pressure of spiropentane was about 300 millimeters of mercury absolute.

The positions of all but the weakest bands are listed in table I in units of microns and inverse centimeters. The uncertainty of the positions varied from about ± 5 cm^{-1} at lower frequencies to ± 10 cm^{-1} for frequencies above 2000 cm^{-1}. Raman frequencies from reference 2 are included for the sake of comparison and completeness. Similarities of the spectra are especially evident but the differences, which are an essential basis for infrared analysis of binary or ternary mixtures by the method of reference 10, may also be discerned and interpreted. A strong band at approximately 10 microns (where, according to reference 6, cyclopropane also absorbs) characterizes spiropentane; whereas strong absorption appears at approximately 6 microns only in the spectra of the other two compounds, each of which contains a double bond. The rather intense band at 7.24 microns in the spectrum of 2-methyl-1-butene has no counterpart in the spectrum of spiropentane nor does methylenecyclobutane have a resolvable band at this wave length. In the three spectra small relative shifts in the positions of other bands are evident. The outstanding similarities are the strong bands at about 3.4 and 11.4 microns that appear in all three spectra.

DISCUSSION

In general, a molecule containing n atoms has (3n-6) normal modes of vibration; accordingly 33 such fundamentals would be predicted for the two C_5H_8 isomers and 2-methyl-1-butene should have 39. Some of these vibrations will be infrared-active, others will be Raman-active, and some will probably be active in both Raman and infrared spectra. Symmetry in a molecule is associated with coincidence or degeneracy of some fundamental frequencies, hence, probably fewer than 33 different bands would be detected in infrared and Raman spectra for each molecule. The lists of approximately 20 different frequencies (not necessarily all fundamentals) for each molecule in table I probably include nearly all resolvable normal vibrations, and possibly a few overtones and combinations. Some intense bands may represent two or more overlapping fundamentals.

In the spectra of methylenecyclobutane and 2-methyl-1-butene, the bands at about 6 microns may be associated with vibrations of the C=C bond. The 10-micron absorption by spiropentane is characteristic of a vibration in the cyclic carbon skeleton of this molecule. Cyclopropane also shows absorption in this region, although it does not have a band at exactly 10 microns. (See reference 6.) Absorption of medium intensity at about 8.6 microns occurs in the spectra of both compounds that have closed rings but it is absent in the spectrum of 2-methyl-1-butene. Absorption at approximately 3.4 microns in all three spectra is characteristic of C-H type vibrations. The bands in the vicinity of 880, 1170, 1430, 1670, and 2960 cm^{-1} are both infrared- and Raman-active in the molecules of which they are characteristic.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, June 25, 1946.

REFERENCES

1. Slabey, Vernon A.: The Synthesis of Methylenecyclobutane, Spiropentane, and 2-Methyl-1-butene from Pentaerythrityl Tetrabromide. NACA TN No. 1023, 1946.

2. Murray, M. J., and Stevenson, Eugene H.: The Debromination of Pentaerythrityl Bromide by Zinc. Isolation of Spiropentane. Jour. Am. Chem. Soc., vol. 66, no. 5, May 1944, pp. 812-816.

3. Donohue, Jerry, Humphrey, George L., and Schomaker, Verner: The Structure of Spiropentane. Jour. Am. Chem. Soc., vol. 67, no. 2, Feb. 1945, pp. 332-335.

4. Bauer, S. H., and Beach, J. Y.: The Structures of Methylenecyclobutane and Hexamethylethane. Jour. Am. Chem. Soc., vol. 64, no. 5, May 1942, pp. 1142-1147.

5. Shand, W., Schomaker, Verner, and Fischer, J. Rodney: The Structures of Methylenecyclobutane and of 1-Methylcyclobutene. Jour. Am. Chem. Soc., vol. 66, no. 4, April 1944, pp. 636-640.

6. Bonner, L. G.: The Infrared Absorption Spectra of Cyclopropane and Ethylene Oxide. Jour. Chem. Phys., vol. 5, no. 9, Sept. 1937, pp. 704-706.

7. King, Gilbert W., and Armstrong, Robert T.: The Vibrational Levels of Cyclopropane. Jour. Am. Chem. Soc., vol. 58, no. 9, Sept. 1936, pp. 1580-1584.

8. Barnes, R. Bowling, McDonald, Robert S., Williams, Van Zandt, and Kinnaird, Richard F.: Small Prism Infra-Red Spectrometry. Jour. Appl. Phys., vol. 16, no. 2, Feb. 1945, pp. 77-86.

9. McAlister, E. D., Matheson, G. L., and Sweeney, W. J.: A Large Recording Spectrograph for the Infra-Red to 15μ. Rev. Sci. Instr., vol. 12, no. 6, June 1941, pp. 314-319.

10. Cleaves, Alden P., and Sherrick, Mildred E.: Infrared-Spectrophotometric Analysis of Binary and Ternary Mixtures of Liquid Hydrocarbons. NACA ARR No. E5F27, 1945.

TABLE I

WAVE LENGTHS AND WAVE NUMBERS OF BANDS IN INFRARED SPECTRA AND WAVE NUMBERS OF SHIFTS IN RAMAN SPECTRA OF SPIROPENTANE METHYLENECYCLOBUTANE, AND 2-METHYL-1-BUTENE

[Raman data taken from reference 2.]

Spiropentane			Methylenecyclobutane			2-Methyl-1-butene		
Infrared		Raman	Infrared		Raman	Infrared		Raman
microns	cm^{-1}	cm^{-1}	microns	cm^{-1}	cm^{-1}	microns	cm^{-1}	cm^{-1}
								252
		305			354			393
		531			373			433
		613						465
					657			530
								709
12.80	781	779	13.20	758		12.75	784	773
11.46	873	872	11.38	879	873	11.25	889	890
10.05	995		9.82	1018	907	9.95	1005	964
					957			1020
9.49	1054	1033	9.32	1073		9.30	1075	1091
8.62	1160	1150	8.55	1170	1191			
			8.00	1250		8.09	1236	
7.48	1337	1397			1391	7.24	1381	1390
								1413
6.96	1437	1426	6.98	1433	1428	6.87	1456	1433
			5.95	1680	1679	6.05	1653	1654
5.68	1761		5.70	1755		5.60	1786	
5.30	1887							
4.87	[a]2050		4.75	[a]2100		4.90	[a]2040	
4.40	2270							
4.29	2330		4.31	2320		4.27	2340	
		2836			2826			2856
		2891			2861			2893
					2902			2917
					2921			2942
3.40	2940		3.33	2960	2952	3.37	2970	2971
		2991			2986			2984
		3065			3072			

[a]Wave-number values above 2000 have only three significant figures.

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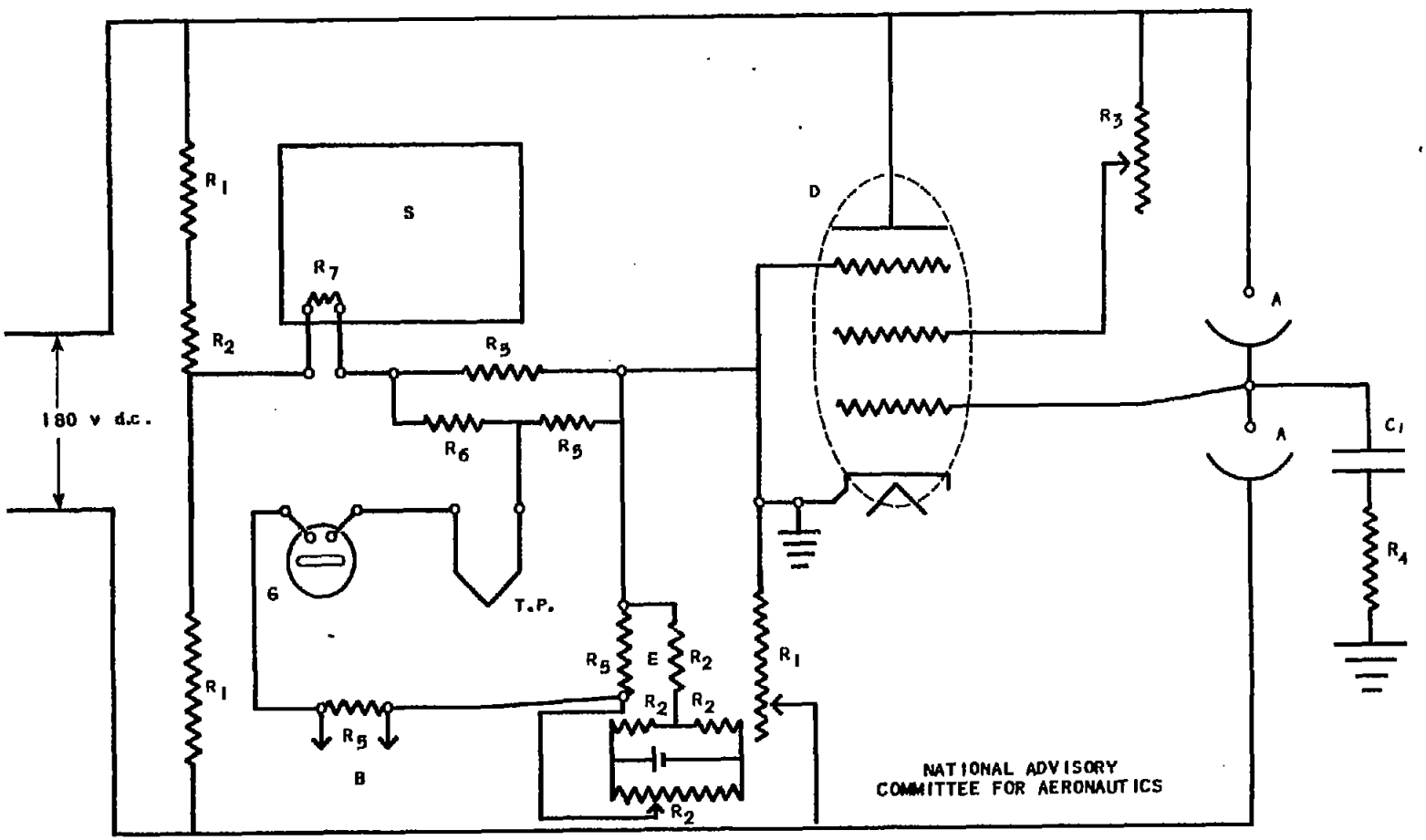
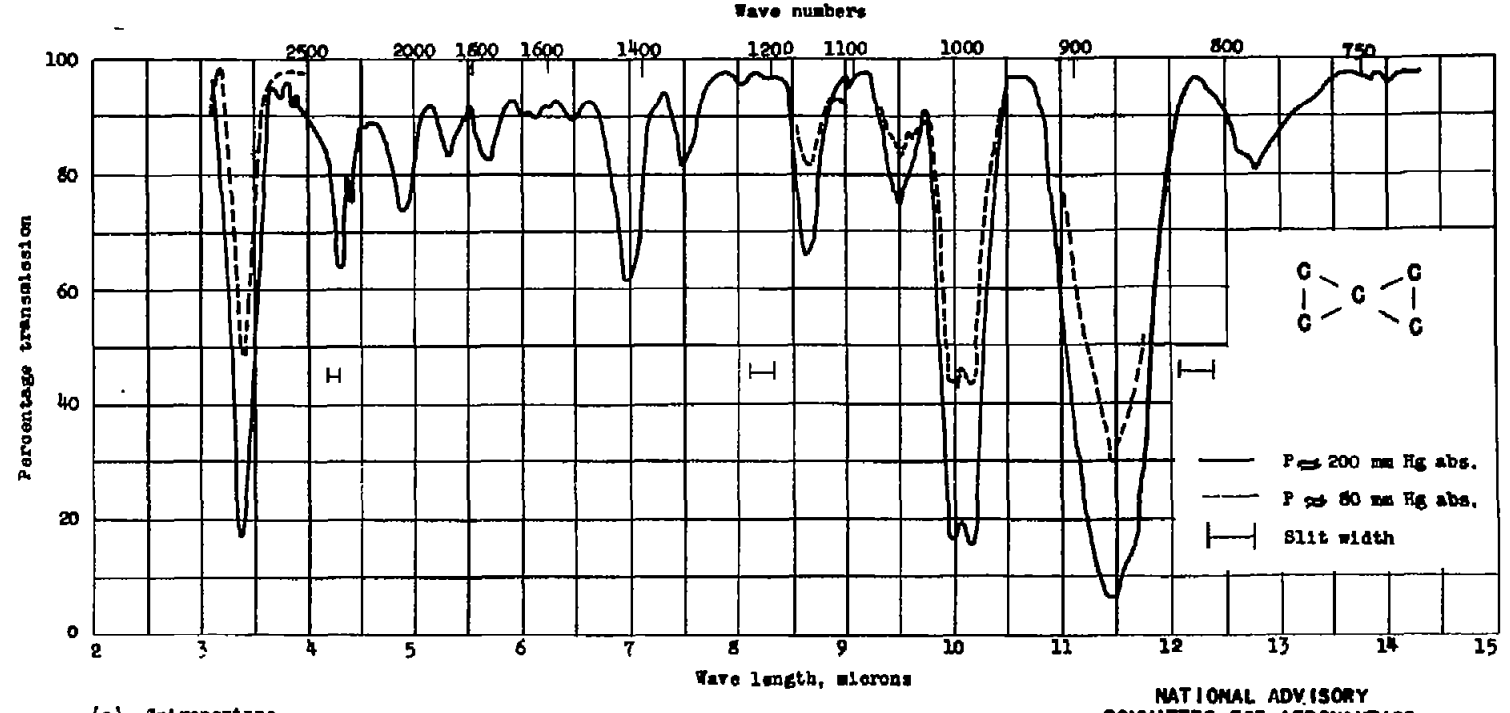


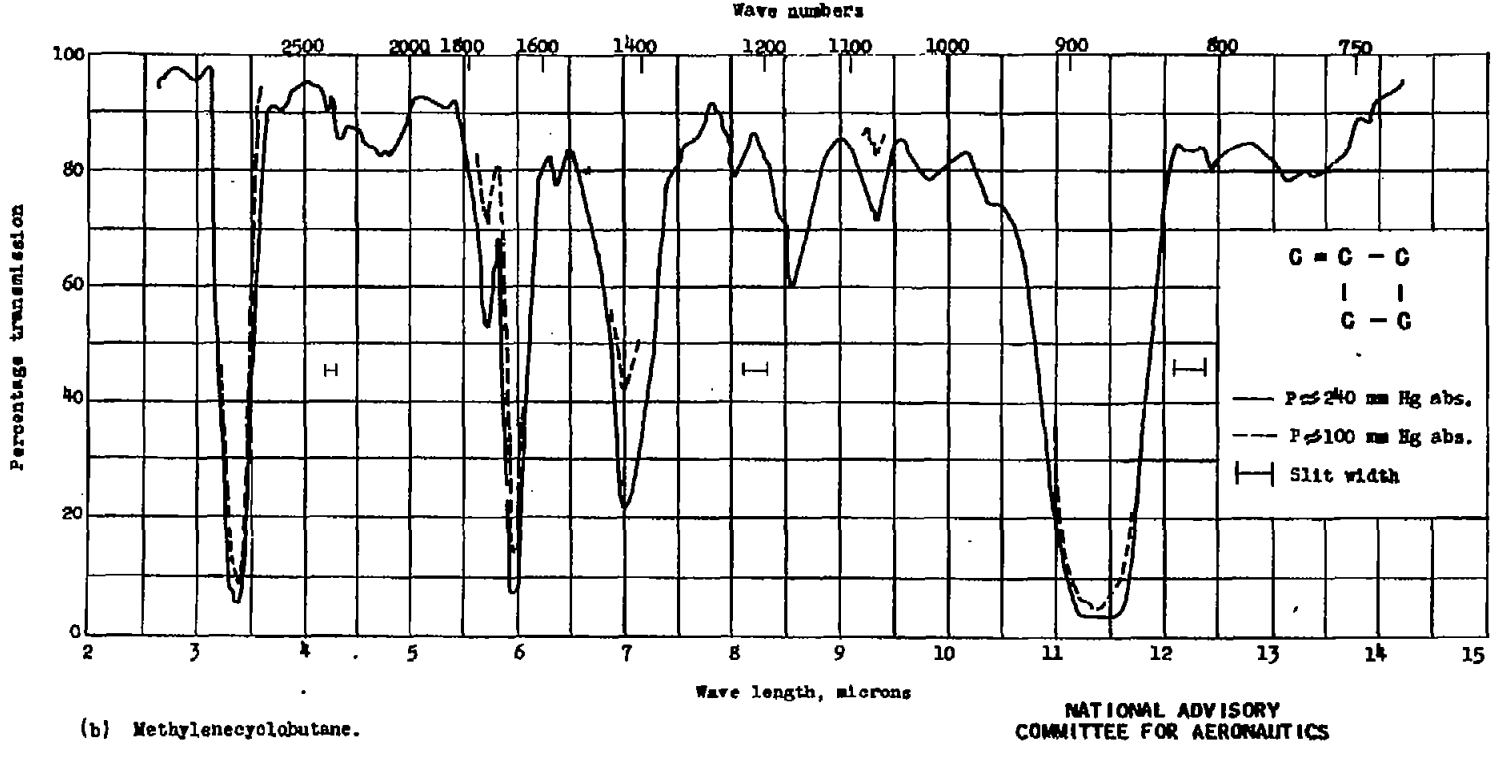
		OHMS			OHMS
A Twin photocells RCA 925	R_1	10,000	E Zero shifter	R_3	20,000
B Input for calibration emf	R_2	1,000	G High-sensitivity galvanometer	R_4	10^7
C Condenser 0.05 mfd	R_7	.75	T.P. High-sensitivity thermopile	R_5	0.01
D Amplifier tube 6G6G			S Speedomax recorder	R_6	.40

Figure 1. – Circuit diagram of twin photocell amplifier for recording output of thermopile in infrared spectrometer.



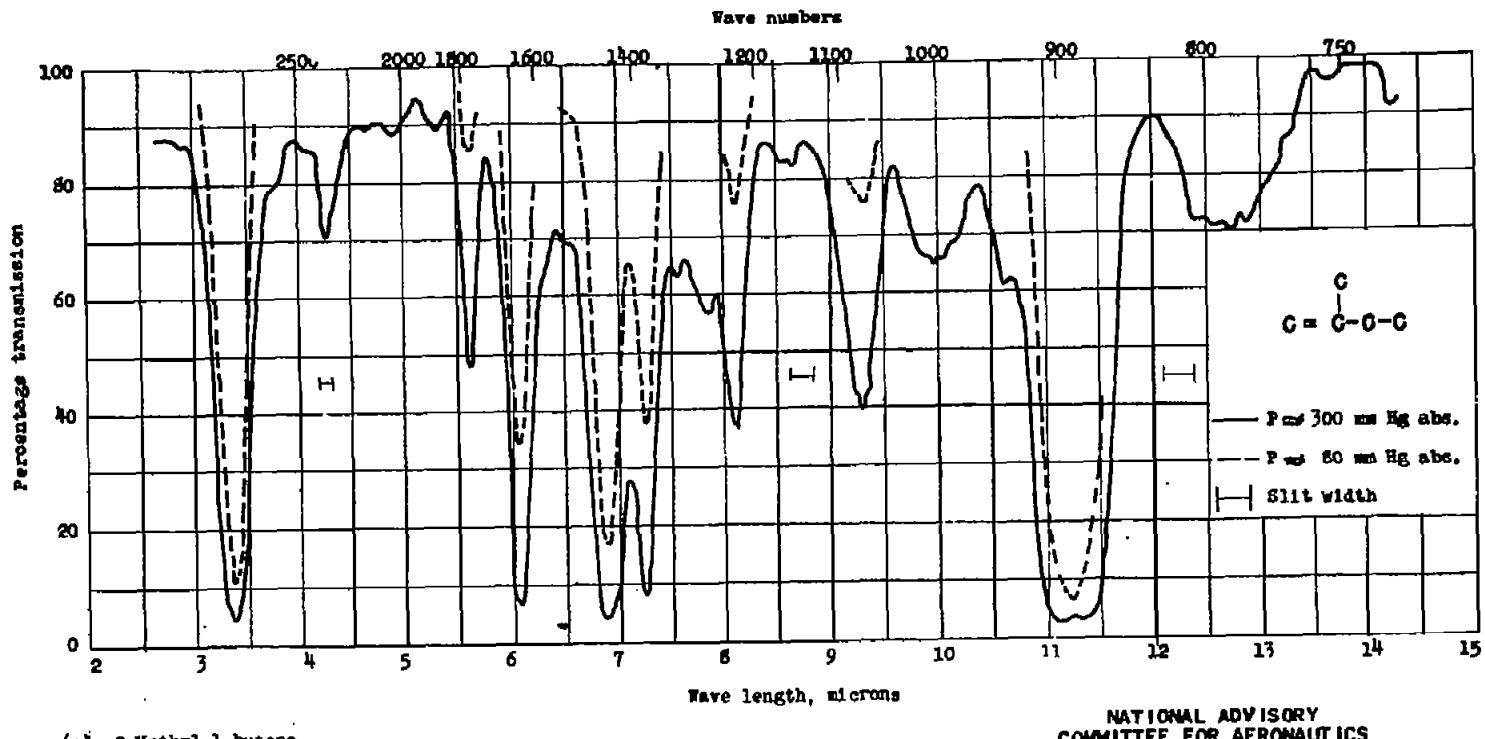
(a) Spiropentane.

Figure 2. - Infrared spectra of vapors in 10-centimeter cell.



(b) Methylenecyclobutane.

Figure 2. - Continued. Infrared spectra of vapors in 10-centimeter cell.



(c) 2-Methyl-1-butene.

Figure 2. - Concluded. Infrared spectra of vapors in 10-centimeter cell.