The ultraviolet absorption of cyclopropane is similar to that of the saturated aliphatic hydrocarbons.

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Cyclopropane: Its Raman Spectrum and Polymerization by Ultraviolet Light

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Introduction

In two recent investigations[1,2] of the Raman spectrum of cyclopropane, the data appear to be incomplete and to contain certain discrepancies. The transparency of cyclopropane to ultraviolet radiation[3] suggested a more favorable technique for the determination of its Raman spectrum. Accordingly, new measurements have been made on both liquid and gaseous cyclopropane.

Apparatus

The Raman cell (Fig. 1) was constructed entirely of clear quartz. It consisted of a Dewar flask with a central tube for confining the sample under investigation. Plane quartz windows of high transmission were sealed to both ends of this tube and to the bottom of the flask. The cell was mounted vertically and the scattered radiation from the central tube was passed into the spectrograph through a totally reflecting quartz prism, necessary precautions being taken to reduce stray light. Five to eight cubic centimeters of liquid cyclopropane sufficed for measurements.

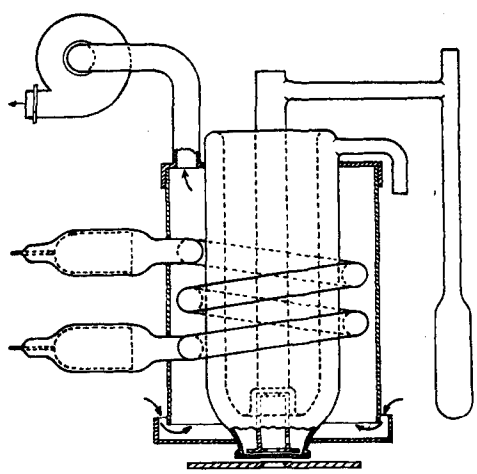

Fig. 1.

The source of exciting radiation was a Hanovia Type SC 2537 mercury lamp in the form of a coil and of such a diameter that it just passed around the Dewar flask. The lamp was operated at 5000 volts with a current of 100 milliamperes, and its light was concentrated on the central tube by a cylindrical aluminum reflector. During operation cooling was effected and the ozone removed by drawing a large volume of air over the lamp.

The radiation of the lamp below 2300 Å. was absorbed by liquid ammonia in the reservoir around the central tube of the cell. This liquid ammonia served also to maintain the cyclopropane below its boiling point. In the measurements on cyclopropane vapor, 25% acetic acid in water was used as the filter.

The spectrum was recorded with a Hilger E 315 quartz spectrograph. Eight-hour exposures sufficed to record the Raman spectrum of the liquid cyclopropane (slit width: 0.02 mm., E. K. No. 33 plates). The iron arc reference spectrum was recorded by passing the radiation down through the Raman cell without disturbing any part of the optical system.

Results

The observed lines are listed in the table.

Observed lines	Frequency displacement (cm.$^{-1}$ from) ν = 39412.26 cm.$^{-1}$	Intensity	L. B. W.[1]	K. K.[2]
2536.52 Å. Hg				
2561.35	382	(v. w.)		
2563.9 Hg				
2576.6 Hg				
2585.4	745	(w.)		
2593.69	869	(v. s.)	867	864
2603.15 Hg				
2604.06	1022	(m.)		
2615.59	1191	(v. s.)	1188	1184
2632.54	1437	(m.)	1439	
2633.70	1454	(m.)		1453
2637.27	1505	(w.)		
2652.07 Hg				
2653.70 Hg				
2655.14 Hg				
2663.1	1873	(v. w.)		
2675.0 Hg				
2698.9 Hg				
2734.75	2856	(w.)		
2741.98	2953	(w.)		
2746.50	3013	(m.)	3011	3008
2747.78	3030	(m.)	3029	3026
2751.48	3079	(m.)	3076	3078
2752.8 Hg				
2760.6	3199 NH_3			
2767.5	3289 NH_3			
2773.7	3770 NH_3			

(1) R. Lespieau, M. Bourguel and R. Wakeman, *Bull. soc. chim.*, [4] **51**, 400 (1932).

(2) K. W. P. Kohlrausch and F. Köppl, *Z. physik. Chem.*, **26B**, 213 (1934).

(3) Ashdown, Harris and Armstrong, THIS JOURNAL, **58**, 850 (1936).

Those lines due to mercury and ammonia are so designated; the remaining lines constitute the the Raman spectrum of cyclopropane. The intensities are designated as strong (s), medium (m) or weak (w). (The last two columns contain previously reported values.)

Under the same conditions of illumination, using the same spectrograph, only the strongest Raman line, 1191 cm.$^{-1}$, appeared in the scattered spectrum of the vapor after seventy-three hours' exposure. Also, several diffuse lines, separated by approximately 28 cm.$^{-1}$, appeared on each side of the 2536 Å. line. The pressure of the cyclopropane in the cell was about 3.5 atmospheres.

Discussion of Results

The agreement of the Raman frequencies found here with those reported by other investigators is within the accuracy of measurement. In addition, seven new frequencies of low intensity are reported. The observation of the two frequencies, 1437 and 1454 cm.$^{-1}$, explains the apparent discrepancy between the two previous reports.

Photosensitized Polymerization of Cyclopropane

During the first attempts to measure the Raman spectrum of the gaseous cyclopropane, the formation of a cloud was observed in the Raman tube during illumination, and after fifty hours of exposure several drops of a colorless liquid had collected in the cell. Such a result was not to be anticipated because the cyclopropane had been found to have no measurable absorption above 2000 Å., even in the liquid state,[3] and the usual precautions to avoid contamination with mercury vapor had been taken. In order to determine whether the new Raman lines observed were due to cyclopropane or to the photochemical product, the phenomenon was studied further.

A quartz cell connected to a mercury manometer was filled with cyclopropane and illuminated with the mercury lamp; all radiation was passed first through at least two centimeters of 25% acetic acid. Under these conditions (cyclopropane, saturated with mercury vapor), the rate of pressure decrease was found to be independent of the initial pressure of the cyclopropane, between 4 and 0.5 atmosphere, and to vary with temperature. The rate of decreasing pressure in the illuminated system at several temperatures, between 0 and 25°, was measured, from which it was found that the rate of pressure decrease was approximately proportional to the vapor pressure of mercury at each temperature. It is therefore concluded that the chemical change is initiated by a mercury-sensitized reaction.[4]

Inasmuch as the Raman spectrum of the liquid was obtained at low temperatures where the vapor pressure of mercury is less than 2×10^{-6} mm., the photosensitized reaction was negligible and none of the observed lines, therefore, were due to products of photochemical change.

Since the pressure diminished continuously (to a value below 10 mm.) the C_3H_6 (cyclopropane) must have been converted to $(CH_2)_x$. The product was a viscous, colorless oil having a boiling point of nearly 300° at 760 mm. and showing continuous absorption in the ultraviolet below 2500 Å.

Summary

The high transmission of cyclopropane to the ultraviolet has made possible the use of the intense 2536 Å. line of mercury for excitation of the Raman spectrum.

The Raman spectrum of cyclopropane consists of fourteen frequencies.

Only one strong line was observed in the Raman spectrum of gaseous cyclopropane. It had the same frequency shift as the strongest line in the liquid.

A mercury-sensitized photochemical polymerization of cyclopropane has been observed under the influence of the 2536 Å. radiation of mercury. The resulting product is a colorless oil of high boiling point.

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(4) Taylor and Bates, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).