[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ORGANIC CHEMISTRY, NO. 136, AND FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 362, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Ultraviolet Absorption of Pure Cyclopropane and Propylene; their Preparation and Boiling Points

BY AVERY A. ASHDOWN, LOUIS HARRIS AND ROBERT T. ARMSTRONG

Introduction

A detailed study of the spectra of cyclopropane and propylene would contribute to the solution of problems arising from the theories of their structure and their chemical relationships as well as form a basis for a study of isomerization by the absorption of light. To obtain data useful for such purposes, extremely pure samples of both cyclopropane and propylene are required. It was necessary to devise methods to yield products of the highest purity and to develop sensitive tests for probable impurities.

Preparation and Purification of Cyclopropane and Propylene and the Boiling Points of the Purified Products

Cyclopropane.—Cyclopropane was prepared by a modification of Gustavson's[1] method. By carefully excluding moisture from the reacting mixture the reduction of trimethylene dibromide to propane is practically eliminated. Freshly distilled trimethylene dibromide (3 mols "E. K. Co.," b. p. 167.8–167.9° at 775 mm.), absolute alcohol (1300 cc.) and zinc wool (4 mols "Kahlbaum") were mixed and gently refluxed in an apparatus, previously dried and protected from atmospheric moisture. The cyclopropane was passed through a trap, cooled to −10° (to retain the small amount of alcohol distilled over), and collected in a reservoir, cooled to −78°. After twenty hours the evolution of cyclopropane became unprofitably slow (125 cc. of liquid collected). This product was distilled once through a column of the Davis[2] type, discarding the initial and final portions. The cyclopropane thus obtained was scrubbed successively with pure bromine, bromine water and then with 30% aqueous potassium hydroxide. After drying over solid potassium hydroxide it was again fractionated by means of the Davis[2] column.

During fractionation temperature measurements of the liquid–vapor were made with the aid of a two-element thermocouple.[3] The finally purified sample of cyclopropane (58 cc. of liquid at −78°) boiled within a range of 0.01°. The observed boiling point was −32.89° at 755.9 mm.

The probable impurities in the cyclopropane were propylene, propane and dissolved air. To determine the combined quantities of the last two substances (together with any other saturated hydrocarbons), measured samples of the cyclopropane were agitated with pure (cold) concentrated sulfuric acid in an apparatus designed for measuring small quantities of gaseous residues. In a typical experiment, 0.51 g. of cyclopropane, after being shaken for ten minutes, yielded a residue of 0.23 cc. (at 27° and 1 atm.) unabsorbed gas. A second test to check this result showed 0.22 cc. of unabsorbed gas. A blank experiment showed 0.03 cc. of unabsorbed gas. It follows that the total residual gas was not more than 0.1% by volume.

The amount of propylene present in the cyclopropane may be estimated from the ultraviolet extinction coefficients of propylene and cyclopropane (see below for details). At 1975 Å. the molecular extinction coefficient of propylene, ϵ, is 12. When liquid cyclopropane, instead of the gaseous propylene, was introduced into the absorption cell, no measurable absorption could be detected at this wave length. It follows, therefore, that the molecular extinction coefficient, ϵ, of cyclopropane is less than 0.0037 at this wave length. The highest possible amount of propylene in the cyclopropane is consequently $0.0037/12 \times 100 = 0.03$ mole per cent. Combining this value with that obtained for the residual gas, the cyclopropane had less than 0.13% total impurity.

Propylene.—Propylene was prepared by refluxing isopropyl alcohol (8.5 mols "E. K. Co.," redistilled, b. p. 82.3–82.6°) with phosphoric acid (26.4 mols, d^{25}_4 1.685).[4] The gas was evolved uniformly, evolution becoming unprofitably slow after eighteen hours. The gas contained a considerable quantity of diisopropyl ether.[5] The propylene, resulting after separation from the ether, had a boiling point range of −47.70 to −47.65° at 758 mm. A middle fraction of this propylene (165 cc. of liquid at −78°) was distilled fractionally in the same column that was used for the cyclopropane. The fraction (65 cc. of liquid) boiling within a temperature range of 0.04° had a mean boiling point of −47.67° at 759.1 mm.

The Ultraviolet Absorption Spectra of Cyclopropane and Propylene

The middle fractions of the purified samples were confined in a quartz cell which had an effective length of 1.5 cm.[6] The liquids were maintained at −78° and the gases at +26 to +27°C. during measurement. Measurements with cyclopropane (gas at room temperature) were also made using a cell with an effective length of 1 meter.

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[1] G. Gustavson, *J. prakt. Chem.*, [2] **36**, 300 (1887).

[2] H. S. Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

[3] No. 36 copper wire and No. 30 constantan wire were used to make the thermocouple of small heat capacity. The e. m. f.s produced were measured with an L. and N. "White" potentiometer in conjunction with an H.S. galvanometer [see Scatchard, Jones and Prentiss, THIS JOURNAL, **54**, 2681 (1932)]. The thermocouple was calibrated at the ice-point, at the boiling point of pure anhydrous ammonia, −33.4 ± 0.01° ["Int. Crit. Tables," Vol. III, p. 234] (calibration carried out under the same conditions as the distillation of cyclopropane), and at the sublimation temperature of solid carbon dioxide.

[4] C. F. Tucker, S.B. Thesis, M. I. T., 1932.

[5] R. Marotta, S.B. Thesis, M. I. T., 1934.

[6] B. J. Eiseman, Jr., THIS JOURNAL, **54**, 1778 (1932).

A Hilger E 315 quartz spectrograph was used to record the spectra for wave lengths greater than 2100 Å., and a Hilger E 370 spectrograph, to record the spectra to 1890 Å., on Eastman type "O" plates. A water-cooled hydrogen discharge tube[7] served as a light source. The light transmissions were evaluated with the aid of calibrated screens, the match points of the spectrograms from the compounds and from the calibrated screens being determined visually. In the case of cyclopropane, wave lengths were determined by a linear interpolation between the successive band heads of atmospheric oxygen. All other wave lengths were measured on the wave length scale (previously calibrated against a copper arc spectrum), accompanying the instrument. By this means, wave length measurements were made with an accuracy of plus or minus two Ångström units, an accuracy within the error of locating match points.

The results are summarized in the plots of ε[8] *versus* λ.

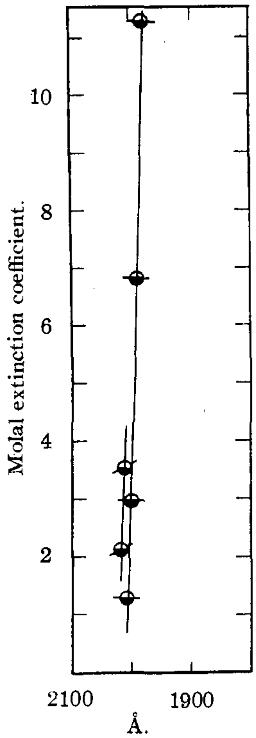

Fig. 1.—Plot of the molal extinction coefficient of propylene (vapor) *vs.* wave length: -⊖-, pressure = 910 mm.; ⊘, pressure = 2910 mm.

Discussion of Results

The value of the normal boiling point of cyclopropane, −32.89 ± 0.05°, obtained in this investigation is well within the range of values reported recently (−32.6 to −33.6°)[9] although quite different from the earlier accepted value, (−34.5°).[10] Likewise, the value found for the normal boiling point of propylene, −47.67 ± 0.1°, lies within the range of the published value, −47.8 ± 0.2°.[11]

The most striking feature of the absorption spectrum of cyclopropane is its high transmission throughout the spectral region 5000 to 1950 Å. Among organic compounds only the saturated aliphatic hydrocarbons possess this property. Propylene, on the other hand, in common with other compounds containing an ethylenic structure, absorbs in the neighborhood of 2400 Å., the absorption increasing rapidly as shorter wave lengths are reached.

The high transmission of the cyclopropane at wave lengths between 1950 and 2200 Å. shows that not more than 0.03 mole per cent of propylene or other ethylenic compounds are present. By the same token, acetylenic and oxygenated compounds are eliminated as impurities.

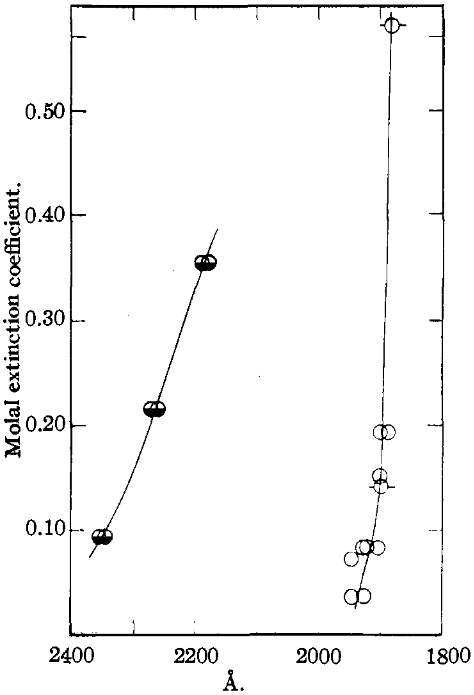

Fig. 2.—Plot of the molal extinction coefficients of cyclopropane and propylene *vs.* wave lengths: ○, cyclopropane, liquid; -○-, cyclopropane, vapor; ⊖, propylene, liquid.

Analysis of mixtures of propylene and cyclopropane can be made advantageously by measuring their extinction coefficients at 2000 Å.

The absorption spectra of both cyclopropane and propylene appear to be continuous to at least 1860 Å.

Summary

Pure samples of cylopropane and propylene have been prepared and their boiling points determined accurately.

Both substances absorb continuously in the ultraviolet. The molecular extinction coefficients of each have been determined.

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(7) Z. Bay and W. Steiner, *Z. Physik*, **45**, 337 (1927).

(8) ε [molecular extinction coefficient] = $(1/cl)$ $(\log I_0/I)$ where c = mols per liter, using ideal gas laws; and for liquids, c was calculated from densities [Trautz and Winkler, *J. prakt. Chem.*, **104**, 37 (1922)]; l = length of cell, cm.; I/I_0 = transmission of respective screens.

(9) Kohlrausch and Köppl, *Z. physik. Chem.*, **B26**, 209 (1934).

(10) Trautz and Winkler, *J. prakt. Chem.*, **104**, 37 (1922).

(11) Burrell and Robertson, Tech. Paper No. 142, U. S. Bureau of Mines (1926).

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

BY LOUIS HARRIS, AVERY A. ASHDOWN AND ROBERT T. ARMSTRONG

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.

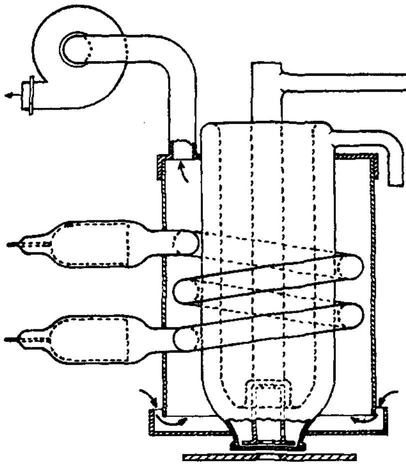

Fig. 1.

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			

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

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

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