[Contribution from the School of Chemistry, University of Minnesota]

THE VAPOR PRESSURE OF ALLENE AS A FUNCTION OF TEMPERATURE

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Since there are at present no data on the vapor pressure of allene available in the literature, it seemed worth while to determine its vapor pressure at a series of temperatures, using a sample of the pure compound which was prepared by one of us (G. B. H.) in connection with a study of its radiochemical and photochemical properties.

The allene was prepared by the action of a suspension of zinc dust on 2,3-dibromo-propene-1. The latter substance was prepared according to the method of Lespieau and Bourguel.[1] The gas was condensed and sealed off in pyrex flasks. One of these flasks was later sealed to the all-glass apparatus and the gas was admitted to the apparatus by means of a magnetic breaking device. The allene was condensed in a liquid-air trap and distilled several times using liquid air as the condensing agent. Any permanent gases present were removed after each condensation by pumping off at a pressure of 10^{-5} mm. The higher-boiling substances were discarded in each distillation and the middle fraction of the final sample was used in this determination

The vapor pressures were measured with an open mercury manometer which was read with an accurate cathetometer. A correction of 1.4 mm. was made for capillary depression. The barometric pressure was recorded at half-hour intervals during the course of the work. The pressure measurements were reproducible within 0.2 mm. The tube containing the liquid allene was surrounded by a Dewar flask filled with an ether–alcohol mixture. The temperature of this bath was adjusted by adding solid carbon dioxide. The temperature measurements, which were reproducible within 0.1°, were made with an accurate platinum resistance thermometer, which was made and calibrated at the Cryogenic Laboratory of the U. S. Bureau of Mines. The calibrations were checked, at the time these measurements were made, at the ice point, 0.0°, and at the freezing point of carefully purified chloroform, −63.5°.

The observed values of the pressure and temperature are listed in the

Table I

Vapor Pressure of Allene as a Function of Temperature

T, °C.	−76.0	−65.4	−55.7	−45.4	−40.2	−36.5
P, mm. (obs.)	85.1	162.4	278.6	469.9	600.8	703.8
P, mm. (calcd.)	85.1	162.5	279.3	469.9	599.6	709.6

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[1] Lespieau and Bourguel, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. V, p. 49.

first two lines of Table I. Each of these values is the average of five or six independent measurements. It is improbable that the errors in the absolute values of the pressure and temperature are greater than 2 mm. and 0.2°, respectively.

The values of the pressure given in the last line were computed from the linear equation

$$\log P = -\frac{0.05223}{T} \times 20{,}852 + 7.455$$

The constants of this equation were obtained directly from the experimental measurements (not the averaged values) by the "method of averages." This equation yields, by a short extrapolation, a value at the normal boiling point of −35.0°.

Lespieau and Chavanne[2] measured the boiling points of both allene ($H_2C{=\!=}C{=\!=}CH_2$) and allylene ($CH_3C{\equiv}CH$). For allene they obtained a value of −32.0°, three degrees higher than the value presented here. Their work is not presented in sufficient detail to make a criticism of their experimental methods possible. It is noteworthy that their value for allylene (−23.5°) is 4° higher than that based upon the very careful measurements of Maass and Wright.[3] It is not surprising that the vapor pressure equation obtained from the data of Maass and Wright for allylene

$$\log P = -\frac{0.05223}{T} \times 21{,}372 + 7.429$$

differs only slightly from that presented here for the closely related isomer, allene.

Summary

The vapor pressure of pure allene has been measured for the temperature range −76.1 to −36.5,° and these data have been fitted to a linear equation.

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[2] Lespieau and Chavanne, *Compt. rend.*, **140**, 1035 (1905).

[3] Maass and Wright, THIS JOURNAL, **43**, 1098 (1921); "International Critical Tables," **1928**, Vol. III, p. 217.