[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, UNITED STATES DEPARTMENT OF AGRICULTURE]

Vapor Pressures of Fumigants. V. α,β-Propylene Dichloride[1]

BY O. A. NELSON AND H. D. YOUNG

Apparently the boiling point and the density or specific gravity of propylene dichloride, as reported in chemical handbooks, are taken from the determinations made by E. Linnemann in 1871.[2] This investigator prepared the α,β- and β,β-propylene dichlorides in the laboratory and purified them by fractional distillation.

It is unlikely that the fractionating stills in use more than sixty years ago were as efficient as those available today. The same may be said of the accuracy of the thermometers then in use. Linnemann determined the boiling point at 736 mm. and, after making the proper corrections, the boiling point reported was 96.83°. The specific gravity was reported as 1.1656 at 14°. The authors undertook not only to check these constants, but to determine the vapor pressure–temperature relationship. Since the boiling point of the α,β-propylene dichloride, which is the one with which we are concerned, is about 10° higher than that of the α,α, 27° higher than the β,β, and 29° lower than the α,γ, it was thought that a product of high purity could be prepared by careful fractional distillation.

Purification of Experimental Material.—Considerable quantities of the purest grade of propylene dichloride obtainable on the market were secured for this work.

The purification of a sample (1500 cc.) was accomplished by means of a 32-plate rectifying still, under a pressure of 165 mm.[3]

From a volume of 1500 cc., 319 cc., or 21.3%, distilled over before the temperature became constant, after which 1098.0 cc. distilled at a constant temperature of 51.7° at 165 mm. The pressure in the fractionating column was kept constant within 1 mm. by means of a monostat. At this pressure $\Delta T = 0.5°/\text{mm.}$

The boiling point determinations were made by means of the apparatus designed by Swietoslawski[4] and previously used by the authors,[5] and the temperature was read by means of Anschütz thermometers recently calibrated at the Bureau of Standards. Corrections were made for pressure when this was not 760 mm. and for emergent stem. The correction for the emergent stem of the thermometer was checked by determining the boiling point of water. The boiling point of the material dried over

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(1) Original manuscript received August 31, 1932.

(2) Linnemann, *Ann.*, **161**, 62 (1871).

(3) The authors wish to thank Dr. S. Palkin of the Industrial Farm Products Laboratory for the use of his fractionating column during the purification of this material.

(4) Swietoslawski, *J. Chem. Ed.*, **5**, 469 (1928).

(5) Young and Nelson, *Ind. Eng. Chem., Anal. Ed.*, **4**, 67 (1932).

phosphorus pentoxide was found to be 96.4° and the density 1.1545 g./cc. at 20°.[6]

Vapor Pressure Measurements.—The pure material obtained from the purification process described above was used in vapor pressure determination. The method used was the same as has been discussed in our previous papers in this series. The results obtained are given in Table I.

TABLE I

Temp., °C.	Interpolated pressure, mm.	Temp., °C.	Interpolated pressure, mm.	Temp., °C.	Interpolated pressure, mm.
10	. . .	45	126.3	80	459.3
15	33.0	50	154.7	85	539.1
20	42.0	55	188.0	90	630.5
25	54.0	60	227.4	95	733.5
30	67.5	65	273.0	96	754.0
35	84.0	70	326.8	96.4	760.0
40	103.5	75	388.0	99.7	847.1

For the preparation of this table the observed temperatures and pressures were plotted on 20 × 30 inch coördinate paper and the recorded pressures read at 5° intervals from the smoothed curve.

The equation $\log P_{\text{mm.}} = 7.7085 - (1782.8/T \text{ abs.})$ was found to give values that did not deviate by more than $\pm 0.5\%$ from the observed pressures up to 850 mm.

The latent heat of vaporization of α,β-propylene dichloride was calculated at two temperatures. The integrated form of the well-known Clapeyron equation was used for this purpose, assuming that the heat of vaporization remains constant over short ranges of temperature. The value for L between 25 and 45° was found to be 8191.4 cal./mole and between 65 and 85°, 8164.4 cal./mole.

For fumigating operations it is of importance to know the quantity of fumigant that can vaporize into a given volume. In our previous publications the equation $W = pM/T$ abs. was developed for the calculation of the weight in pounds (W) that could vaporize into 1000 cu. ft. of space. M is the molecular weight (in the case of propylene dichloride it is 112.98), p is the pressure in millimeters of the compound at the absolute temperature T. Some values calculated for the lower temperatures are given below.

T, °C.	20	25	30	35
Lb./1000 cu. ft.	16.3	20.7	25.1	30.7

Summary and Conclusions

α,β-Propylene dichloride, the principal constituent of the commercial product, has been carefully purified, and accurate determinations of its

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[6] Assuming that Linnemann's determination of specific gravity should read 1.1656^{14}_{4} and an average coefficient of expansion, the two determinations are in close agreement. The boiling points are also in fair agreement.

density, its boiling point at 760 mm. and its vapor pressure at different temperatures up to its boiling point have been made. The boiling point was found to be 96.4° at 760 mm. and the density 1.1545 g./cc. at 20°. The vapor pressure conforms well to the equation $\log P_{\text{mm.}} = 7.7085 - (1782.8/T \text{ abs.})$.

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Oxyacids of Fluorine. II

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In a "Communication to the Editor"[1] we briefly described experiments that seemed to indicate the formation of an oxyacid of fluorine when fluorine is passed into a solution of cesium carbonate or of the hydroxides of potassium, lithium or calcium, and also upon the passage of the gas into a suspension of calcium carbonate in water.

The research has been continued, and although it is as yet by no means completed, a brief report upon its progress is here given.

Fluorination of Aqueous Solutions.—Wartenberg and Klinkott state[2] that in their study of the reactions

$$2F_2 + 2NaOH \text{ (dilute)} = 2NaF + H_2O + F_2O$$
$$F_2O + 2NaOH \text{ (concentrated)} = 2NaF + H_2O + O_2$$

they found no evidence of the formation of a salt of an oxyacid of fluorine.

In their interesting investigations of oxidation with fluorine, Fichter and Bladergroen[3] passed fluorine into a cold, concentrated solution of potassium hydroxide and observed that the solution had oxidizing power, which they ascribed to the formation of potassium ozonate. Baeyer and Villiger, however, state[4] that potassium ozonate has no oxidizing action. Traube later found[5] that when solid potassium hydroxide is subjected to long treatment with ozone at about −12° and is then dissolved in ice-cold sulfuric acid and titrated with potassium permanganate, a fraction of 1% of hydrogen peroxide is present.

It seems reasonable to assume that the action of fluorine upon a cold solution of an alkali hydroxide is analogous to that of chlorine, and that the first stage of the reaction is

$$F_2 + 2NaOH = NaFO + NaF + H_2O$$

the unstable sodium hypofluorite then slowly breaking down with the liberation of F_2O

$$2NaFO + H_2O = 2NaOH + F_2O$$

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(1) THIS JOURNAL, **54,** 832 (1932).

(2) Wartenberg and Klinkott, *Z. anorg. allgem. Chem.*, **193,** 409 (1930).

(3) Fichter and Bladergroen, *Helv. Chim. Acta*, **10,** 549 (1927).

(4) Baeyer and Villiger, *Ber.*, **35,** 3038 (1902).

(5) Traube, *ibid.*, **45,** 2201 (1912).