Summary

1. Diphenylnitrosamine in liquid ammonia solution reacts with the amides of lithium, sodium, potassium and calcium in accordance with the equation $R_2NNO + 2MNH_2 \longrightarrow R_2NM + MOH + N_2 + NH_3$.

2. Di-*p*-tolylnitrosamine reacts similarly with sodium and potassium amides.

3. Dibenzylnitrosamine and methylphenylnitrosamine do not react with potassium amide in accordance with the above equation.

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[Contribution from the Chemical Laboratories of the University of Minnesota and Northwestern University]

Vapor Pressure and Boiling Point of Pure Methylacetylene*

By G. B. Heisig and Charles D. Hurd

Methylacetylene was required by one of us (G. B. H.) for a study of its condensation in the presence of alpha particles. A sample of the gas prepared and purified in the usual way by distilling to a constant vapor pressure at a fixed temperature gave vapor pressures much lower than those reported by Maass and Wright[1] or calculated from their data using the equation given in the International Critical Tables.[2]

$$\mathrm{Log}\,P_{\mathrm{mm.}} = (0.05223/T) \times 21{,}372 \times 7.429$$

The logarithms of the pressures plotted against the reciprocal of the absolute temperatures gave a straight line which by extrapolation gave a boiling point of approximately −23°. This value agreed with the boiling point of −23.5° reported by Lespieau and Chavanne[2a] rather than that of −27.5° obtained by Maass and Wright. A second sample was prepared and gave similar results.

Meinert and Hurd[3] then reported a boiling point of −23° for pure methylacetylene. Davis, Crandall and Higbee[4] noted that the boiling point was higher than −27.5° and listed it as −20 to −18°. In an effort to obtain a purer product and a sample which could not contain acetylene, sodium acetylide was methylated by the action of methyl sulfate according to the method of Meinert and Hurd. About 10 cc. of product obtained by this method was distilled through a Davis column.[5] A fraction boiling between −22 and −25° was collected which when distilled a second time boiled at −23°. After distilling twice from a container maintained at the

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(1) Maass and Wright, This Journal, **43**, 1101 (1921).

(2) International Critical Tables, Vol. III, p. 217 (1928).

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

(3) Meinert and Hurd, This Journal, **52**, 4544 (1930).

(4) Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 109 (1931).

(5) Davis, *ibid.*, **1**, 61–64 (1929).

temperature of carbon dioxide, condensing in liquid air, and retaining only the middle portion, the vapor pressure was determined. After six more distillations carried out in this way the vapor pressure did not change. Vapor pressure measurements were made at a number of temperatures on this sample. Later Glockler and Davis[6] used the low and high boiling portions of the original sample to obtain Raman spectra and reported a line corresponding to the unweighted acetylene bond.

Instead of purifying this methylacetylene more rigorously (to exclude acetylene) it was decided to synthesize it by a method which would use no acetylene, namely, by interaction of propylene bromide and alcoholic sodium hydroxide.[7] All but about 1% of the allene which was produced concurrently was removed by fractionation in the Davis column. Three methods of purification were employed from this point: (1) precise fractional distillation through a Podbielniak column.[8] By this means 1 cc. of distillate boiling below −23° was removed. Another 2-cc. portion was discarded before collecting 42 cc. which was saved. It distilled in entirety at −23° without the fluctuation of a fraction of a degree. We are indebted to F. D. Pilgrim and A. R. Goldsby for assistance in this synthesis and distillation. (2) Conversion to the cuprous salt by passing the gas into an ammoniacal solution of cuprous chloride and, after thorough washing, decomposing the salt with a slight excess of hydrochloric acid. The gas was liquefied, led through wash bottles filled with water and sodium hydroxide, and distilled through a Davis column. Next it was dried by passing over calcium chloride and finally over phosphorus pentoxide on glass wool. (3) Conversion of the methylacetylene to the sodium methylacetylide by sodium in liquid ammonia and the evaporation of all of the ammonia and traces of allene under reduced pressure. The residue was redissolved in liquid ammonia and the methylacetylene regenerated by the action of an equivalent quantity of ammonium chloride. The effluent gas was thoroughly washed with 5% sulfuric acid containing methyl orange so the last two wash bottles never became alkaline, and dried by passage over calcium chloride and finally over phosphorus pentoxide.

Samples purified by each of these methods were distilled to constant vapor pressure in liquid air traps. The vapor pressures of each of the three specimens were identical at −79.2° and at −28.1°. The vapor pressure of the sample (A) prepared by the action of sodium acetylide and methyl sulfate was 2.5% higher at −28.1° and about 18% higher at −79.2° than that of the purified methylacetylene (B) made from propylene bromide. If sample (A) had been purified by fractionation through the Podbielniak column it would undoubtedly have attained the purity which was reached in (B). The identity of the vapor pressure at a given tempera-

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[6] Glockler and Davis, private communication.

[7] Hurd, Meinert and Spence, THIS JOURNAL, **52**, 1141 (1930).

[8] Podbielniak, *Oil Gas J.*, **28**, 38 (1929); **29**, 235 (1930).

ture of the methylacetylene (B) purified by three different methods is convincing evidence of its purity. No precipitate was formed in an ammoniacal solution of cuprous chloride containing ammonium chloride after standing four hours. In addition, it gave no test for a halide. Finally, the vapor density determined by the method of Maass and Russell[9] was 39.95 as compared with a theoretical value of 40.

The vapor pressure of the sample purified by converting to the cuprous salt was determined at ten temperatures. The sample was placed in a container immersed in a low temperature thermostat, to be described elsewhere. The temperature was maintained within ±0.01° and was measured by a platinum resistance thermometer which was calibrated at the Cryogenic Laboratory of the U. S. Bureau of Mines. Pressures were measured with an accurate cathetometer. At least five readings were made at each temperature. The maximum variation between readings was 0.2 mm. The data were fitted to the equation

$$\text{Log } P_{\text{mm.}} = (-1247.95/T) + 7.877$$

and the calculated pressures corresponding to the various temperatures are found in column 3 in Table I. In column 4 the percentage variation between calculated and observed values are given.

TABLE I

VAPOR PRESSURE OF METHYLACETYLENE

T, °C.	$P_{\text{obs.}}$, mm.	$P_{\text{calcd.}}$, mm.	% difference	T, °C.	$P_{\text{obs.}}$, mm.	$P_{\text{calcd.}}$, mm.	% difference
−79.5	26.7	27.0	+1.1	45.6	249.9	246.3	−1.4
75.2	37.1	37.2	+0.3	38.7	361.6	358.5	−0.9
71.0	49.3	50.2	+1.8	33.0	478.2	478.0	−0.0
64.2	80.7	80.1	−0.7	27.8	612.3	614.5	+0.4
52.5	169.6	167.2	−1.4	23.5	743.5	754.3	+1.5

The boiling point calculated by means of this equation is −23.1°.

Summary

Pure methylacetylene has been prepared. Its vapor pressure at several temperatures has been determined and the data have been fitted to an equation by means of which the boiling point has been calculated and found to be −23.1°.

MINNEAPOLIS, MINNESOTA
EVANSTON, ILLINOIS

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[9] Maass and Russell, THIS JOURNAL, **40**, 1847–1852 (1918).