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The extrapolated boiling point is −17.1°, and the vapor pressures at −78.5° (28 mm.), −63.5° (73 mm.), and −45.2° (210 mm.) may be used as criteria of purity. The infrared spectrum of the gas has been reported;[6] the appearance of a band at 1252 cm.$^{-1}$ indicates the presence of methyl iodide, and the appearance of a band at 1170 cm.$^{-1}$ indicates the presence of dimethyl ether.

The methylphosphine prepared by this procedure has a vapor pressure at −78.5° (Dry Ice slush) of 29 mm. The principal impurity is dimethyl ether, estimated by mass spectrometry and infrared spectrometry to amount to less than 1%.

References

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26. DIMETHYLPHOSPHINE

$$2KOH + PH_3 \rightarrow K^+ + PH_2^- + KOH \cdot H_2O$$
$$CH_3I + PH_2^- \rightarrow CH_3PH_2 + I^-$$
$$2KOH + CH_3PH_2 \rightarrow K^+ + CH_3PH^- + KOH \cdot H_2O$$
$$CH_3I + CH_3PH \rightarrow (CH_3)_2PH + I^-$$

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The following procedure is adaptable to the synthesis of 0.05 mole, or less, of dimethylphosphine. The procedure described on p. 157 may be used for the synthesis of larger quantities.

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Procedure

■ ***Caution.*** *Phosphine and the methylphosphines are toxic materials which must be handled with great care, using vacuum-line manipulation. Dimethyl sulfoxide should not be allowed to contact the skin because it is absorbed very rapidly.*

The procedure is the same as that used for the preparation of methylphosphine up to the point where the methyl iodide solution is added. A solution of 1.5 ml. (0.024 mole) of methyl iodide in 10 ml. of dimethyl sulfoxide is placed in the dropping funnel, and the stopcock connecting the system to the vacuum line is closed. Sufficient methyl iodide solution is added, during a period less than 1 minute, to decolorize the solution. If, during the addition, the pressure in the flask exceeds 600 mm., the volume of the system should be increased by opening the stopcock to an evacuated volume of several hundred milliliters so as to keep the pressure below 600 mm. However, the volume of the system should not be unduly expanded, or the deprotonation of the methylphosphine will proceed too slowly. The slurry is vigorously stirred for an hour, during which time the pressure of methylphosphine should markedly decrease. Then the remainder of the methyl iodide solution is added (leaving a drop of solution to ensure that air does not enter the flask), and stirring is continued for another half-hour. The volatile material is collected in a liquid-nitrogen-cooled trap and is then fractionally condensed in traps cooled to $-78°$ (Dry Ice slush), $-112°$ (CS_2 slush), and $-196°$ (liquid nitrogen). The material which collects in the -78 and $-196°$ traps is discarded. The dimethylphosphine in the $-112°$ trap usually contains an appreciable amount of methyl iodide as an impurity. However, this impurity may be readily eliminated by simply allowing the mixture to stand in the liquid state at 0° for about one hour, during which time the methyl iodide is converted to the relatively nonvolatile salt, $(CH_3)_3PHI$. About 0.0078 mole (65% yield) of purified dimethylphosphine remains.

Properties

Like methylphosphine, dimethylphosphine has a disgusting odor and is probably very poisonous. The vapor pressure may be represented[1] by the equation $\log P(\text{mm.}) = 7.539 - 1370/T$, where $T = °K$. The extrapolated boiling point is 21.1°, and the vapor pressure at 0° (338 mm.) may be used as a criterion of purity. Dimethylphosphine prepared by this procedure has a vapor pressure at 0° of 339 mm.

Dimethylphosphine can be converted to trimethylphosphine by treatment with excess methyl iodide at 0° to form $(CH_3)_3PHI$, followed by reaction with potassium hydroxide to liberate the trimethylphosphine. The latter step is readily accomplished by adding a dimethyl sulfoxide solution of $(CH_3)_3PHI$ to a slurry of potassium hydroxide in dimethyl sulfoxide *in vacuo*.

Reference

1. N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 718 (1942).

27. METHYLGERMANE

$$2KOH + GeH_4 \rightarrow K^+ + GeH_3^- + KOH \cdot H_2O$$
$$CH_3I + GeH_3^- \rightarrow CH_3GeH_3 + I^-$$

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As in the case of alkylphosphines (see the preceding two syntheses), alkylgermanes are generally prepared by either of two methods: a method based on the deprotonation and subsequent

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