

ing values at 410°: toluene, 33.6 cal. per mole degree; cyclohexane, 37.3; and methylcyclohexane, 44.5. With the exception of cyclohexane, these values are lower than the results found in this investigation. Other investigators have obtained higher results than Bennewitz and Rossner for acetone,¹² heptane and pentane.¹³

Discussion

For the more complex organic molecules, which have not yet yielded to the methods of calculating heat capacity from spectroscopic data, semi-empirical equations for the calculation of heat capacity have great practical importance. An excellent general equation is the one which was proposed by Bennewitz and Rossner¹¹ and modified by Fugassi and Rudy¹⁴ and by Dobratz.¹⁵ In this equation, the vibrational contribution to heat capacity is calculated by means of the Einstein functions, using valence-bonding frequencies evaluated from Raman spectra and deformation frequencies empirically calculated from experimental data.

(12) De Vries and Collins, unpublished data.

(13) Pitzer, *THIS JOURNAL*, **62**, 1224 (1940); *ibid.*, **63**, 2413 (1941).

(14) Fugassi and Rudy, *Ind. Eng. Chem.*, **30**, 1029 (1938).

(15) Dobratz, *ibid.*, **33**, 759 (1941).

Heat capacities calculated with the modified equation of Dobratz are represented in Table II. The agreement with toluene, fluorobenzene, cyclohexane and cyclohexene is not very satisfactory. In both the aromatic and alicyclic series the calculated results are relatively lower for the compounds in which the ring symmetry has been destroyed by substituted groups. The discrepancy between the experimental and calculated results suggests that the empirically assigned deformation frequencies should be corrected to bring the calculated values into closer agreement with recent experimental data. Further work is in progress on this problem.

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Summary

Measurements have been reported for the heat capacities of benzene, fluorobenzene, toluene, cyclohexane, methylcyclohexane and cyclohexene vapors at atmospheric pressure from their boiling points to 410°K.

The experimental results have been compared with semi-empirically calculated heat capacities.

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The Preparation and Physical Properties of Trimeric Phosphonitrilic Chloride

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The phosphonitrilic chlorides, which may be represented by the empirical formula PNCl_2 , may be looked upon as the ammonio analogs of phosphoryl chloride. Like their aquo analog they are capable of undergoing a wide variety of solvolytic reactions. However, they differ from phosphoryl chloride in their ability to undergo polymerization with formation of compounds of high molecular weight, some of which resemble rubber in appearance and properties. In addition to these highly polymerized forms a series of stable polyhomologs is known ranging from $(\text{PNCl}_2)_3$ to $(\text{PNCl}_2)_7$.

The preparation of the phosphonitrilic chlorides involves the partial ammonolysis of phosphorus pentachloride. Ammonia,¹ ammonium chloride and ammonobasic mercuric chloride² have

been employed as ammonolytic agents. However, only ammonium chloride has been used successfully, first by Stokes,³ who heated mixtures of the reactants in closed tubes under pressure, and later by Schenck and Römer,⁴ who employed *s*-tetrachloroethane as a medium for the reaction. Mixtures of the various polyhomologs are always obtained.

It has also been reported by Besson and Rosset⁵ that phosphonitrilic chlorides may be obtained by heating together equimolecular quantities of phosphorus pentachloride and ammonium chloride; in other words, neither solvent nor reaction under pressure are necessary. Unfortunately, neither yields nor conditions are specified by

(1) Liebig and Wöhler, *Ann.*, **11**, 139 (1834).

(2) Gladstone and Holmes, *J. Chem. Soc.*, **17**, 226 (1864).

(3) Stokes, *THIS JOURNAL*, **17**, 275 (1895); **19**, 782 (1897).

(4) Schenck and Römer, *Ber.*, **57B**, 1343 (1924).

(5) Besson and Rosset, *Compt. rend.*, **143**, 37 (1906).

these investigators. A careful study of all three procedures led to choice of the Besson and Rosset method, after the influence of ratio of reactants and of temperature conditions had been determined. The present paper describes the preparation of the phosphonitrilic chlorides, the separation and the purification of the trimer and a study of the vapor pressure of the latter over the temperature range 75.2 to 189.3°.

Experimental

Preparation of the Phosphonitrilic Chlorides.—The equation $\text{PCl}_5 + \text{NH}_4\text{Cl} \longrightarrow \text{PNCl}_2 + 4\text{HCl}$ indicates that the extent and speed of the reaction can be determined readily by observing the rate of evolution of hydrogen chloride and by weighing the reaction product. All experiments were carried out in 50-cm. test-tubes made from 35 or 50-mm. Pyrex tubing. Intimate mixtures of phosphorus pentachloride, 52.1 g. (0.25 mole), and varying quantities of ammonium chloride (25 to 100 g.) were placed in the bottom of the tube and then covered with a capping of ammonium chloride one to three inches in thickness. The tube was immersed in an oil-bath to such a depth that the ammonium chloride cap was kept largely above the liquid level. The outlet to the reaction tube was connected to a trap containing sulfuric acid.

Heating was continued at bath temperatures varying from 120 to 160° until the evolution of hydrogen chloride had practically ceased. During the course of the reaction considerable amounts of the trimer were observed to sublime and collect in the cooler portions of the reaction vessel. On the basis of a large number of experiments optimum yields of trimer-tetramer fractions are obtained if the bath temperature is kept between 145 and 160°. A heating time of four to six hours is necessary to achieve 90–95% conversion to the phosphonitrilic chlorides.

After completion of the reaction, the residue was extracted with low-boiling petroleum ether (50–70°) which removes quantitatively the trimeric and tetrameric homologs. Evaporation of the solvent yielded mixtures of these corresponding to 38 to 43% of theory based upon the amount of phosphorus pentachloride used. Using the amounts specified above, 11 to 12.5 g. of the trimer-tetramer mixture was obtained consistently.⁶

(6) After the trimer and tetramer have been removed, the higher polyhomologs can then be obtained from the residue by extraction with benzene, carbon tetrachloride or chloroform. Evaporation of these solutions invariably resulted in the formation of thick, viscous oils or rubbery solids. This extraction also removes the unreacted phosphorus pentachloride, and it is the opinion of the authors that

For preparation of the pure trimer it was necessary to distill fractionally the mixture under reduced pressure to give a trimer-rich fraction (12–14 mm. with a bath temperature of 140°). This product was then recrystallized by solution in a minimum amount of hot 100% acetic acid and subsequent cooling. It was then further purified by repeated fractional sublimation at $100 \pm 5^\circ$ at a pressure of one mm. or less. Products prepared in this manner were used for the determination of the vapor pressure.

Vapor Pressure of Trimeric Phosphonitrilic Chloride.

The apparatus and method employed in the measurement of the vapor pressures of trimeric phosphonitrilic chloride were those previously described by Laubengayer and Schirmer.⁷ Two series of measurements using different samples were carried out representing a total of 37 readings whose maximum deviation from calculated values, with one exception, amounted to ± 0.5 mm. with an average deviation of 0.2 mm. A plot of these results as a function of $\log p$ and $1/T$ gives two straight lines which represent the solid-vapor and the liquid-vapor equilibria, the equations for these lines being

$$\log p = -3978(1/T) + 11.187 \quad (\text{where } t = 75.2 - 114.9)$$

and

$$\log p = -2880(1/T) + 8.357 \quad (\text{where } t = 114.9 - 189.3)$$

respectively. The intersection of these curves, the triple point, representing the melting point of the trimer, corresponds to a temperature of 114.9°. This agrees well with the value 114° reported by other investigators.^{3,4} The normal boiling point obtained by extrapolation of the liquid-vapor curve to 760 mm. pressure is 252.7° which is somewhat lower than the previously accepted value 256° reported by Stokes⁸ in 1897.

The molal heat of vaporization calculated from the slope of the liquid-vapor curve is 13.2 kilocalories; the molal heat of sublimation calculated from the slope of the solid-vapor curve is 18.2 kilocalories; and the molal heat of fusion obtained by difference is 5.0 kilocalories.

Summary

1. A simplified procedure for the preparation of the phosphonitrilic chlorides is described.
2. The trimer has been carefully purified and its vapor pressure determined over the temperature range 75.2 to 189.3°.

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the presence of this material causes extensive polymerization to take place.

(7) Laubengayer and Schirmer, *THIS JOURNAL*, **63**, 1578 (1940).