

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Vapor Pressure of Phenylhydrazine as a Function of the Temperature¹

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Work now in progress in this Laboratory required a knowledge of the vapor pressure and latent heat of vaporization of phenylhydrazine. A search of the literature revealed an almost total lack of information based on any adequately purified and protected sample. The present work was therefore undertaken to obtain the required data over a considerable range of temperature.

Procedure and Apparatus.—The isotenoscopic apparatus of Smith and Menzies² was used, suitably modified so that samples could be introduced by distillation at reduced pressure and protected during the experimental manipulation in an atmosphere of dry nitrogen. Temperatures were controlled to $\pm 0.02^\circ$ and the thermometers had been compared with standards calibrated by the National Bureau of Standards. The manometer was of the Germann³ design and was read to 0.1 mm. with a cathetometer, the readings being corrected to 0° , sea level, and latitude of 45° .

As a check on the accuracy of the procedure, the vapor pressure of water was measured in the temperature range 20 – 75° , and that of aniline in the range 100 – 150° . The arithmetical mean deviation of the twelve measurements with water was ± 0.24 mm., with a maximum deviation of ± 0.40 mm. The results for aniline agreed with the data of Ramsay and Young⁴ rather than with those of Garrick,⁵ obtained with a different type of apparatus unsuitable for use with phenylhydrazine. The maximum deviation of our experimental points from the smoothed values of Ramsay and Young at eight temperatures was 0.8 mm., the mean being ± 0.3 mm.

Materials.—The nitrogen supply was passed through sodium pyrogallate to remove oxygen, and dried over a long column of calcium chloride and "anhydron." The phenylhydrazine was prepared by the method of Coleman⁶ and purified by fractionation under reduced pressure (18 mm.) in an atmosphere of nitrogen. The middle fraction from 250 cc. was distilled onto crushed stick sodium hydroxide. After standing, the phenylhydrazine was redistilled and a 20-cc. middle fraction was introduced into the isotenoscope. Four different samples were used including one from the Eastman Kodak Company. All were purified in the same manner. The aniline (Eastman Kodak Company) was purified in essentially the same manner as the phenylhydrazine.

Results and Discussion.—Fifty-five values of the vapor pressure were obtained between 100

and 192° using the four samples. Some sets of readings were taken with falling temperatures and some rising. It was found that these data fitted well an empirical equation of the form used by Cox⁷ and Davis⁸ and shown by them to be valid with a considerable variety of substances over a range of 340° . This equation is essentially $\log P = A - B/(t + 230)$, where t = centigrade temperature and P is the pressure in mm. Utilizing the 50 experimental points between 105 and 150° , the values of the constants A and B of this equation were derived by the method of least squares and found to be as follows: $A = 7.9046$; $B = 2366.4$.

The arithmetical mean deviation of the vapor pressures calculated by this formula from those observed was ± 0.4 mm., with a maximum deviation of ± 1.0 mm. In terms of percentage, the mean deviation above 125° was $\pm 1.0\%$, while at lower temperatures the smaller absolute values of the vapor pressure (7 – 17 mm.) resulted in a larger mean deviation, approximately 3.0% .

As a further test of the adequacy of the equation, the vapor pressures measured at the five higher temperatures in the range 160 – 192° were compared with those calculated. The average arithmetical mean deviation of these measurements was ± 0.7 mm. or $\pm 0.5\%$, the maximum deviation being $+0.75\%$. This showed that a fit, practically equal to the precision of the measurements was afforded by this equation.

The normal boiling point of phenylhydrazine calculated from the equation was 241° , slightly lower than the highest value given in the literature,⁹ but in good agreement with others.

For the estimation of the latent heat of vaporization, values of the vapor pressure were calculated at 10° intervals, and from adjacent pairs the latent heat was calculated by the Clausius-Clapeyron equation, which is the best approximation that can be had, lacking critical data. The results are shown in Table I.

(1) Based on Thesis for the Master's Degree by G. E. Williams, 1942. Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 66, School of Science.

(2) Smith and Menzies, *THIS JOURNAL*, **32**, 897, 997, 1412 (1910).

(3) Germann, *ibid.*, **36**, 2456 (1914).

(4) Ramsay and Young, *J. Chem. Soc.*, **47**, 640 (1885).

(5) Garrick, *Trans. Faraday Soc.*, **23**, 560 (1927).

(6) "Organic Synthesis," Coll. Vol. I, second edition, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 442.

(7) Cox, *Ind. Eng. Chem.*, **15**, 592 (1923).

(8) Davis, *ibid.*, **17**, 735 (1925); **22**, 380 (1930).

(9) Perkin, *J. Chem. Soc.*, **69**, 1209 (1896); Blanksma, *Chem. Weekblad.*, **7**, 418 (1910); Fischer, *Ann.*, **236**, 198 (1896); Heilbron, "Dictionary of Organic Compounds," Oxford University Press, N. Y., 1938, Vol. 3, p. 419.

TABLE I

THE HEAT OF VAPORIZATION OF PHENYLHYDRAZINE

Temp., °C.	25	95	105	115
	125	135	145	240
Heat of vaporization, cal./mole	(14690)	13886	13788	13693
	13610	13526	13455	(12903)

Summary

The vapor pressure of phenylhydrazine has been measured by means of the isoteniscope over

the range 105–192° with a precision of about ± 0.4 mm. From the resulting data an empirical equation was derived by the method of least squares which reproduced these values to within the experimental precision.

From these values of the vapor pressure the latent heat of vaporization at temperatures from 25–240° has been computed and tabulated.

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Kinetics of the Transformation of Hydrazine Cyanate into Semicarbazide¹

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The transformation of ammonium cyanate into urea has been the subject of numerous and exhaustive studies but the analogous reaction of hydrazine cyanate to form semicarbazide has never been subjected to critical examination. Such examination is complicated by the reactive nature of the substances involved and also by the fact that semicarbazide is definitely basic whereas urea is so weakly basic that for practical purposes its proton affinity in dilute aqueous solution is entirely negligible. The present work, however, represents a study of the kinetics of the reaction, simple salt effects, equilibrium measurements and the effect of temperature on the rate.

Experimental Part

Preparation of Materials.—Potassium Cyanate (Baker C. P.) was suspended in absolute ethanol by vigorous shaking, to dissolve any small amount of cyanide present. It was then collected on a filter, washed with ether and dried. It was then preserved in a vacuum desiccator and stored in the dark. Prepared in this manner, analysis by the Volhard method showed a purity of 99.6%.

Two neutral salts of hydrazine, the perchlorate and monohydrochloride, were prepared from Kahlbaum 100% hydrazine hydrate and the corresponding pure acids. These salts were recrystallized from 80% methanol and dried over sulfuric acid. They were analyzed by the iodate method.

For equilibrium measurements semicarbazide was necessary. Eastman Kodak Co. semicarbazide hydrochloride was recrystallized from 80% methanol, and checked for purity by Volhard analysis for chloride content. Foreign salts added to increase ionic strength were Baker C. P. quality.

Procedure.—The unexpected rapidity of the reaction precluded the preparation of pure hydrazine cyanate (free from other ions) from silver cyanate and hydrazine chloride in a manner analogous to that used by Warner and Stitt² to prepare ammonium cyanate.

All solutions were made up by adding hydrazine monochloride or perchlorate in solution to exactly equivalent amounts of potassium cyanate. This was accomplished by a vessel of special design which permitted almost instantaneous mixing of small amounts of these solutions. Measurements were made at 25 and 15° in a bath controlled to $\pm 0.05^\circ$.

The progress of the reaction was followed by withdrawing samples which were added to excess standard silver nitrate solution. The precipitated silver salts were filtered out and the excess silver ions in an aliquot portion were determined by titration with standard thiocyanate using ferric alum indicator.

From these results the amount of unreacted cyanate present at any time was calculable.

Equilibrium measurements were made from both forward and backward directions. Reaction mixtures of hydrazine and cyanate were allowed to react until the cyanate titer was constant. Similarly semicarbazide solutions of equivalent concentrations were allowed to stand at constant temperature and analyzed for cyanate from time to time. Equilibrium lies so far toward completion that the reverse reaction has no detectable effect in the early stages of the process.

Discussion

The rapidity of the reaction as measured was quite unexpected as the laboratory directions for the preparation of semicarbazide by this method³ called for elevated temperature and twenty to twenty-four hours of standing. It was therefore thought desirable to demonstrate that the reaction being followed was actually that which was postu-

(1) Taken from the thesis presented by Elton M. Baker in partial fulfillment of requirements for the Ph.D., Oregon State College, 1942. Published with the approval of the Monographs Publication Committee, O. S. C. Research Paper 67.

(2) Warner and Stitt, *THIS JOURNAL*, **55**, 4807 (1933).

(3) Beilstein, 4th edition, Vol. III, p. 98.