quots (5 cc.) of the reaction mixtures were titrated with standard acid to determine the concentration of the reagent. After refluxing for the desired time, the reaction product was titrated with standard acid. Per cent. reaction given by reagent 2 was determined by a Volhard titration for chloride ion. Under these conditions silver nitrate does not attack s-butyl chloride.

Physical Properties.—Boiling points were determined in a modified Cottrell apparatus.[6] Temperatures were read on high precision thermometers graduated in 0.2° (Double Diamond, H. B. Instrument Co.) and pressures were corrected.

Densities were measured with pycnometers of about 5-cc. capacity. All determinations were checked by running each compound in two different pycnometers. The instruments were calibrated with triply-distilled water.

Discussion

The data of Table II on the neosilicon chlorides are in line with results previously reported for a comparison of the reactivity of silico-neopentyl chloride (chloromethyltrimethylsilane) with that of n-hexyl chloride.[2]

These data show that the inertness of the *primary* alpha C–Cl bond in silico-neopentyl chloride toward silver nitrate reagents[2] is paralleled by that of *secondary* C–Cl bonds alpha to silicon. This inactivity of secondary neosilicon chlorides is even more unusual than that of silico-neopentyl chloride. Although secondary alkyl chlorides are more reactive than primary alkyl chlorides with silver nitrate, secondary C–Cl bonds alpha to silicon are *less* reactive with these reagents than are primary C–Cl bonds in ordinary alkyl chlorides. This is further evidence for the strong electronegativity of neosilicon groups, since reagents such as silver ion act with organic chlorides by attacking the halogen together with its shared electron pair (electrophilic attack on halogen).[7] Reaction mixture (5) which acts with alkyl chlorides

by the same mechanism (electrophilic attack on halogen by a solvent),[8] is also far less effective with the neosilicon chlorides than with s-butyl chloride. Results with this reaction mixture are thus in complete agreement with those obtained from reaction mixtures (6) and (7).

Results with reaction mixtures 1–4, which act with alkyl halides *via* a rearward attach mechanism (bimolecular nucleophilic reactions), show that the neosilicon halides are somewhat less reactive here than is s-butyl chloride. However, the differences in reactivity are generally much less than with reaction mixtures 5–7. This parallels the differences in reactivity with similar reagents of silico-neopentyl chloride and n-hexyl chlorides.[2] α-Chloroethyldiethylphenylsilane is the most reactive of the neosilicon chlorides. α-Chloroethyldiethylsilanol is more reactive than the neosilicon chlorides. Thus substitution of alkyl on silicon by phenyl or hydroxyl increases the activity of an alpha C–Cl bond.

Summary

1. Seven new chloroalkyl silanes have been prepared.

2. α-Chloroethyldiethylsilanol, the first example of a chloroalkyl silanol, is unusually stable toward intermolecular dehydration.

3. The beta C–Cl bonds in β-chloroethyldiethylchlorosilane and in β-chloroethyldiethylfluorosilane are broken by titration with 0.2 N alkali with the formation of ethylene by beta fission.

4. Further studies on the alpha silicon effect provide additional evidence for the action of silicon as an electron sink.

STATE COLLEGE, PENNA   RECEIVED[9] JUNE 10, 1946

(6) Quiggle, Tongberg and Fenske, *Ind.-Eng. Chem., Anal. Ed.,* **6**, 466 (1934).

(7) For a more complete discussion of the theoretical significance of these results, see ref. 2.

(8) Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, pp. 153–155 and 166–167.

(9) Original manuscript received November 16, 1945.

The Pressure–Volume Relations of the Gaseous Methylamines at 0° and Reduced Pressures

BY J. C. ARTHUR[1] WITH W. A. FELSING

Introduction.—The deviation from ideality of a gas may be calculated by obtaining an equation which relates the pressure–volume product to the pressure. Experimentally determined densities constitute the data for such an equation. This Laboratory has concerned itself with the thermodynamic properties of the methylamines[2]

but has not determined the deviations at low pressures. Such data have not previously been reported in the literature; their determination has been the object of this investigation.

Method Used.—The method of this investigation of the determination of the minimum densities of the gaseous methylamines is based upon a procedure proposed by Maass and Russell[3] and

(1) Présent address: Southern Regional Research Laboratory, New Orleans, La.

(2) (a) Felsing und Thomas, *J. Ind. Eng. Chem.,* **21**, 1269 (1929); (b) Felsing and Wohlford, THIS JOURNAL, **54**, 1442 (1932); (c) Felsing and Breckley, *J. Phys. Chem.,* **37**, 779 (1933); (d) Felsing and Jessen, THIS JOURNAL, **55**, 4418 (1933); (e) Felsing and Ashby, *ibid.,* **56**, 2226 (1934); (f) Felsing and Phillips, *ibid.,* **58**, 1973 (1936);

(g) Patterson with Felsing, *ibid.,* **60**, 2693 (1938); (h) Kenner with Felsing, *ibid.,* **61**, 2451 (1939); (i) Felsing and Ball, *ibid.,* **63**, 2525 (1941); (j) Jones, Spubler with Felsing, THIS JOURNAL, **64**, 965 (1942); (k) Whitlow with Felsing, *ibid.,* **66**, 2028 (1944).

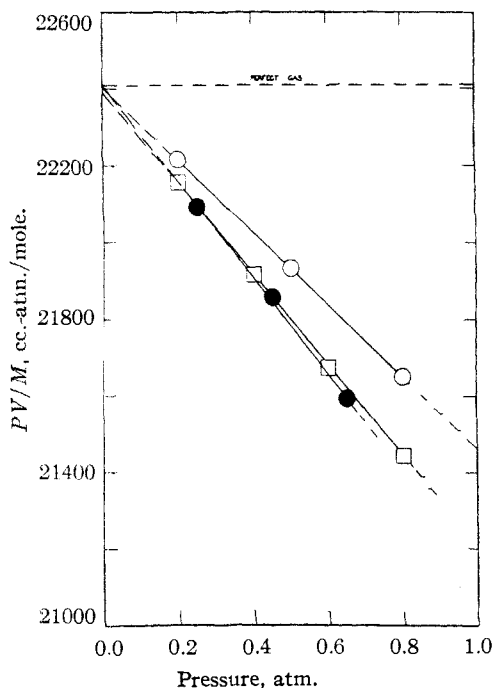(3) Maass and Russell, *ibid.,* **40**, 1847 (1918).

Fig. 1.—Variation of molar pressure–volume product with pressure at 0°: O, monomethylamine; ●, dimethylamine; □, trimethylamine.

modified by Dietrichson, Bircher and O'Brien.[4] This method, in brief, consisted of the determination of the pressure, at constant temperature, of a large volume of gas and of condensing this large volume of gas into a small bulb whose weight is of the same order of magnitude as that of the gas. In modifying the method, it was assumed that the adsorption effect could be eliminated by bringing the gas down to varying final bulb pressures during the condensation process. According to the adsorption law, the total amount adsorbed tends to approach a *constant* saturation value at relatively low pressures, provided a true adsorption effect is involved. Thus, as the residual pressure is made progressively larger, the condensed liquid should represent material drawn only from the gas phase. According to this modified procedure, the problem develops into a determination of limiting minimum density with increasing residual pressure. It was by this modified method that Dietrichson, Orleman and Rubin[5] determined the densities of ammonia gas under reduced pressures and from the data thus obtained, established the relationship of the pressure–volume product to the pressure. The details of the apparatus and the method can be gotten from the literature cited and from a thesis.[6]

Materials.—The mono-, di- and trimethylamines were prepared from the hydrochlorides.

(4) Dietrichson, Bircher and O'Brien, THIS JOURNAL, **55**, 1 (1933).

(5) Dietrichson, Orleman and Rubin, *ibid.*, **55**, 14 (1933).

(6) J. C. Arthur, M. A. Thesis, "The Deviation from Ideality of the Gaseous Methylamines," The University of Texas, June, 1946.

Eastman Kodak Co. C. P. salts were highly purified by the methods following. (a) **Monomethylamine hydrochloride:** this salt was subjected to Soxhlet extraction with chloroform to remove the soluble di- and trimethylamine hydrochlorides and was then further purified by successive crystallizations of the extracted portion in ethanol. **Dimethylamine hydrochloride:** this salt was recrystallized three times from anhydrous chloroform. **Trimethylamine hydrochloride:** this salt was recrystallized once from chloroform and twice from *n*-propyl alcohol. The gaseous amines were prepared by treatment, in an appropriate generator[2a] of the purified salts with an excess of 50% potassium hydroxide solution. The liberated gases were dried over metallic sodium; they were condensed into and stored in steel cylinders until used.

The Data and their Treatment.—The experimentally determined values of the limiting minimum density and pressure are shown in Table I. The values of the limiting minimum density were determined by plotting the residual pressure *versus* the experimentally determined values of density and observing the minimum density as the residual pressure was increased. The weight of gas in the apparatus at the residual pressure was estimated by the perfect gas law. Using this approximate value of density, a preliminary equation of state was computed. The corrected weight of gas in the apparatus was then determined by this equation.

The corrected density values were plotted *versus* the residual pressure. From these minimum density and pressure values, the pressure–volume products were related by an equation of the type

$$PV = A + BP + CP^2$$

the pressure–volume product *per mole* being used to facilitate the comparison of the deviations from ideality of each gas. The data are estimated correct to within 0.10% at the higher pressures and to within 0.20% at the lower. The values of PV/M (= 22,412 cc./atm. for an ideal gas at 0°.) are expressed as functions of the pressure in Table II and are shown in Fig. 1.

TABLE I

MINIMUM DENSITY VALUES AND PRESSURE–VOLUME PRODUCTS PER GRAM AND PER MOLE OF THE GASEOUS METHYLAMINES AT 0°

Amine gas	Press., atm.	$D_{min.}$ g./liter	P/DP cc.-atm./g.	PV/M, cc.atm./mole
Monomethyl	0.2	0.2796	715.308	22,216.4
	.5	.7080	706.215	21,934.0
	.8	1.1476	697.107	21,651.2
Dimethyl	.25	0.5102	490.004	22,091.3
	.45	.9282	484.809	21,857.1
	.65	1.3569	479.068	21,596.7
Trimethyl	.2	0.5336	374.813	22,155.5
	.4	1.0790	370.714	21,913.2
	.6	1.6363	366.681	21,674.5
	.8	2.2054	362.746	21,442.2

Gas	PV/M cc.-atm./mole	Valid range, atm.	Deviation coef., λ
CH_3NH_2	22,404–942 atm.	0–1.000	−0.0420
$(CH_3)_2NH$	22,413–1,254	0–0.737	−0.0560
$(CH_3)_3N$	22,393–1,188	0–0.895	−0.0531

The valid range was determined by the value of the vapor pressure of the liquid amine at 0°; thus the vapor pressures are 1.349, 0.737[7] and 0.895 atmospheres for the mono-, di- and tri-methylamines, respectively.

The deviation coefficient was evaluated by

(7) Swift and Hochanadel, Proc. Indiana Acad. Sci., 54, 121 (1945).

means of the relation proposed by Dietrichson, Orleman and Rubin[5] at constant temperature

$$\lambda = \frac{1}{(PV)_{P \to 0}} \times \frac{\partial (PV)}{\partial P}$$

Summary

The densities of the gaseous methylamines have been determined at 0° and at pressures ranging from 0.2 to approximately 0.8 atm.

The equations of state at 0°, the limiting molar volumes and the deviation coefficients have been evaluated.

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The Nature of the N–H Bond in the Porphyrins[1]

BY J. GORDON ERDMAN[2] AND ALSOPH H. CORWIN

Since the discovery of the phenomenon of "hydrogen bridging" there has been discussion as to whether or not the bond is symmetrical with the hydrogen midway between the other two atoms involved. In general, it has been concluded that these bonds are unsymmetrical.[3] A peculiarly favorable case for symmetrical bonding exists in the porphyrins, for although a pair of adjacent nitrogens and a hydrogen cannot form a straight line, the nitrogens are close enough to permit symmetrical placement of the hydrogens and are constrained in their positions by large forces which are independent of the hydrogen bonds. The present paper is an attempt to find by gross examination of spectra whether or not the bonding is symmetrical.

An alternative to hydrogen bonding has been proposed in the case of the porphyrins. Corwin and Quattlebaum[4] suggested that N isomerism might possibly exist with hydrogens attached in some cases to adjacent nitrogens. They pointed out that the formation of acid salts or metallo complexes would result in "resonance" isomers and consequent interconversion of the two forms. They believed that in view of the short N–H–N distance, hydrogen bridging might play a part in porphyrin structure and suggested the synthesis and study of N-methyl porphyrins to settle the question.

Opinion is still divided between the hypothesis of N isomers and that of hydrogen bridging.

Robertson,[5] Vestling and Downing[6] and Aronoff and Weast[7] after physical studies favor the hypothesis of hydrogen bridging. On the other hand Rothemund[8] and Rothemund and Menotti[9] in their syntheses of porphyrin and the $\alpha,\beta,\gamma,\delta$-substituted porphyrins from pyrrole and aldehyde obtained pairs of presumably isomeric porphyrins which could be separated by acid fractionation. These authors and their collaborators[10] assume these to be N isomers. It should be pointed out that separation by acid fractionation implies that the nitrogens do not become equivalent even in the diacid salt. Stable "resonance" isomers of this type are without analogy in the literature.[11] The fact that N-methyl porphyrins are now available[12] makes it possible to learn more about the nature of the N–H bonding in the ring. The studies reported herewith lead us to conclude that it is unlikely that symmetrical N–H–N bonds exist in the porphyrin ring. A hydrogen atom in a porphyrin ring is probably bonded to a single nitrogen atom at any instant even though it may be within the field of force of the adjacent nitrogen atom at the time.

The Küster formula for porphyrin represents a highly conjugated system, the bond arrangement of which is arbitrary just as in the Kekulé formula for benzene. It is natural to seek to achieve a better representation of the porphyrin structure through superimposition of "Kekulé" and hybrid

(1) Studies in the Pyrrole Series XVII; Paper XVI, Ellingson and Corwin, THIS JOURNAL, 68, 1112 (1946). This paper was presented at the New York Meeting of the American Chemical Society, September, 1944.

(2) Present address: Mellon Institute, University of Pittsburgh, Pittsburgh, Pennsylvania.

(3) See Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 44–51.

(4) Corwin and Quattlebaum, THIS JOURNAL, 58, 1081 (1936).

(5) Robertson, J. Chem. Soc., 1195 (1936).

(6) Vestling and Downing, THIS JOURNAL, 61, 3511 (1939).

(7) Aronoff and Weast, J. Org. Chem., 6, 550 (1941).

(8) Rothemund, THIS JOURNAL, 57, 2010 (1935); 58, 635 (1936); 61, 2912 (1939).

(9) Rothemund and Menotti, ibid., 63, 267 (1941).

(10) Albers and Knorr, J. Chem. Phys., 4, 422 (1936); Knorr and Albers, ibid., 9, 197 (1941).

(11) See Aronoff and Calvin, J. Org. Chem., 8, 205 (1943).

(12) McEwen, THIS JOURNAL, 68, 711 (1946).