TABLE IV

THE DISSOCIATION CONSTANT AND HEAT OF DISSOCIATION OF BORIC ACID

| $t°$ | $pK$(obs.) | $pK$(eq. 4) | $K \times 10^{10}$ | $\Delta H$(cal.) |
|---|---|---|---|---|
| 10 | 9.380 | 9.379 | 4.17 | 3920 |
| 15 | 9.327 | 9.328 | 4.70 | 3750 |
| 20 | 9.280 | 9.280 | 5.25 | 3570 |
| 25 | 9.236 | 9.237 | 5.80 | 3360 |
| 30 | 9.197 | 9.197 | 6.35 | 3140 |
| 35 | | 9.162 | 6.89 | 2900 |
| 40 | 9.132 | 9.131 | 7.39 | 2630 |
| 45 | | 9.103 | 7.89 | 2350 |
| 50 | 9.080 | 9.079 | 8.33 | 2040 |

The internal consistency of the various series points to an accuracy of about ±0.002 in $pK$, or 0.1 mv. in $E - E°$. It should be remarked, however, that Equation (1) would not be strictly applicable if $HBO_2$ shows any considerable tendency to form complexes in the most dilute solutions. The curvature of the lines in Fig. 1 demonstrates the limitations of Equation (1) in this respect,[13] but does not, in the author's opinion, prohibit its use as a practical extrapolation function, especially when $\rho \approx 1$, and the curve is almost horizontal. A variety of investigations[14] indicate complete dissociation of the tetraborate ion into metaboric[15] acid and its ions in dilute solution. Therefore, by virtue of the extrapolation to infinite dilution, the constants in Table IV must pertain to this acid. Increasing concentration of free acid favors the formation of the stronger[14d] tetraboric acid, so at finite concentrations the expression "dissociation constant of boric acid" is ambiguous.[8] A striking demonstration of this increase in acid strength is given in Fig. 1, where the effect of the buffer ratio is many times greater than that which we might normally ascribe to the medium effect of the undissociated acid upon its ions.[16]

## Summary

The dissociation constant of metaboric acid (or the first dissociation constant of orthoboric acid) and the corresponding heat of dissociation have been determined over the temperature range from 10 to 50°. At 25° $K = 5.80 \times 10^{-10}$ and $\Delta H = 3360$ cal.

The results have been expressed as a temperature function in formal agreement with the equations proposed by Harned and Embree[12] for the dissociation of weak electrolytes.

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[13] The same effect can be observed in the presence of "zwitter" ions. *Cf.* Nims and Smith, *J. Biol. Chem.*, **101**, 401 (1933), and Owen, THIS JOURNAL, **56**, 24 (1934).

[14] (a) Noyes and Whitney, *Z. physik. Chem.*, **15**, 694 (1894); (b) Kahlenberg and Schreiner, *ibid.*, **20**, 547 (1896); (c) Shelton, *ibid.*, **43**, 494 (1903); (d) Auerbach, *Z. anorg. Chem.*, **37**, 352 (1904); (e) Schmidt and Finger, *J. Phys. Chem.*, **12**, 406 (1908).

[15] It is unnecessary for our purposes to distinguish between *meta-* and *ortho-*boric acids.

[16] Owen, THIS JOURNAL, **54**, 1758 (1932). Also Ref. 2a.

NEW HAVEN, CONN. RECEIVED JUNE 11, 1934

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

# The Dipole Moments of Phosgene, Hydrogen Cyanide and Certain Substituted Methanes

BY C. P. SMYTH AND K. B. MCALPINE

Determinations of the dipole moments of phosgene, hydrogen cyanide, nitromethane and chloropicrin are reported in the present paper in order that they may be available for discussions of structure. The dielectric constants of the vapors were measured with the apparatus and method previously described,[1] the gold-palladium cell used by Zahn[2] being employed in the measurements. As in the earlier work, the polarization $P$ was calculated from the dielectric constant $\epsilon$ and the molar volume $V$ as $P = [(\epsilon - 1)/(\epsilon + 2)]V$. The errors in $P$ caused by using the ideal gas law to calculate $V$ were eliminated by extrapolating to zero pressure to obtain a value for use in the Debye equation, $P = a + b/T$. Table I gives, at each absolute temperature $T$, the value of the polarization at zero pressure, $P_0$, read from the polarization-pressure curves. These straight lines, usually representing six to ten points, become horizontal at high temperatures. The values of $a$ and $b$, of the atomic polarization, $P_A = a - P_E$, of $P_E$, the molar refraction extrapolated to infinite wave length, and of the moment $\mu$ calculated from $b$ are listed in Table II. The tendency of chloropicrin to decompose made it impossible to run over a range of temperature.

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[1] McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933); *J. Chem. Phys.*, **1**, 190 (1933).

[2] Zahn, *Phys. Rev.*, **24**, 400 (1924).

Consequently, values of $a$ and $b$ could not be obtained for it and the moment was calculated from the difference between the average of several polarization values at one temperature and the molar refraction for the D sodium line. Its moment value may, therefore, be in error by as much as $0.07 \times 10^{-18}$, while the other moments should be in error by no more than $0.01 \times 10^{-18}$.

## Purification of Materials

**Phosgene.**—From a tank of commercial material about 100 cc. of liquid was condensed and allowed to stand over mercury for several weeks to remove free chlorine, after which it was fractionally distilled from a trap. The first 20 or 30 cc. of distillate had a high vapor pressure, probably because of dissolved carbon monoxide, but the remainder that came over had a pressure of 560.4 mm. at 0°, as compared to the value 568.3 mm. obtained by Atkinson, Heycock and Pope.[3]

**Hydrogen Cyanide.**—Anhydrous hydrogen cyanide was prepared by the action of sulfuric acid on sodium cyanide.[4] It was thoroughly dried by passage through calcium chloride tubes and fractionally distilled, almost the entire amount coming over at 26° (762 mm.). Determinations before and after the dielectric constant had been measured gave a vapor pressure 265.0 mm. at 0°.

**Nitromethane.**—Material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled. The fraction boiling at 100.8–101.1° gave, after further drying over phosphorus pentoxide, a fraction boiling at 100.5° (748 mm.), which was used for the measurements; $n_D^{20}$ 1.38195.

**Chloropicrin.**—Material from the Eastman Kodak Company was dried over calcium chloride and distilled at ordinary pressure. The greater portion came over in the range 111.0–111.1° (748 mm.), but it had a slight brownish color suggesting a trace of decomposition. When redistilled under reduced pressure, it came over colorless; $n_D^{20}$ 1.46225. Refractive index measurements before and after the distillation at reduced pressure yielded identical values.

TABLE I

EXTRAPOLATED POLARIZATIONS

| Phosgene | | Hydrogen cyanide | | Nitromethane | |
|---|---|---|---|---|---|
| $T$, °K. | $P_0$ | $T$, °K. | $P_0$ | $T$, °K. | $P_0$ |
| 302.6 | 46.76 | 301.3 | 182.5 | 339.0 | 231.5 |
| 323.3 | 45.04 | 338.0 | 163.5 | 380.7 | 208.5 |
| 349.2 | 43.20 | 384.4 | 143.7 | 400.8 | 198.6 |
| 391.1 | 40.40 | 425.6 | 131.4 | 435.1 | 185.0 |
| 425.4 | 38.58 | 470.3 | 119.1 | 448.8 | 179.6 |
| | | Chloropicrin | | 493.2 | 164.9 |
| | | 343.7 | 90.7 | 494.1 | 164.6 |

TABLE II

VALUES OF CALCULATED CONSTANTS

| | $a$ | $P_E$ | $P_A$ | $b$ | $\mu \times 10^{18}$ |
|---|---|---|---|---|---|
| $COCl_2$ | 18.29 | 17.1 | 1.2 | 8625 | 1.18 |
| HCN | 6.32 | 6.31 | 0 | 53060 | 2.932 |
| $CH_3NO_2$ | 18.34 | 12.1 | 6.1 | 72330 | 3.42 |
| $CCl_3NO_2$ | | | | | 1.88 |

## Discussion of Results

The atomic polarization 1.2 found for phosgene is somewhat smaller than most of those found for the halogenated methanes, but of the same order of magnitude. The zero value found for hydrogen cyanide is of interest because, hitherto, only small molecules with small or with no dipoles have shown values of $P_A$ very close to zero.[5] Evidently a single large dipole may be so tightly bound as to give little or no atomic polarization. The value 6.1 for nitromethane is higher than those of the halogenated methanes and, indeed, higher than any previously found in dependable measurements on gases except that for nitrobenzene shortly to be published. Although it is customary to find a considerable atomic polarization in a molecule containing a large dipole, the value for nitromethane is abnormally high. It would be interesting to obtain an accurate value for acetonitrile to determine the effect of the large cyanide moment in a molecule larger than that of hydrogen cyanide.

The moment of the phosgene molecule, $1.18 \times 10^{-18}$, is the resultant of the C=O and the two C—Cl moments, the valence angles and inductive effects, of course, playing their part. Dornte's[6] examination of the phosgene molecule by means of electron diffraction gives the Cl–C–Cl angle as 110 ± 5°, which leaves the usual 125° angles between the double and the two single bonds on the carbon. At first glance, it would seem reasonable to suppose that the $COCl_2$ moment should be equal to the difference between the $CH_2Cl_2$ moment and the $CH_2O$ moment, which has not been determined. However, as far as polarizability is concerned, it is correct to use the acetone moment rather than that of formaldehyde, for the polarizability of the methyl group is close to that of the chlorine.[7] The inductive effect of the C=O dipole on the two chlorines in the phosgene molecule should, therefore, be similar in magnitude to the effect of the C=O on the two methyl groups in the acetone molecule. As the polarizability of the C=O group is equal to that for two C—H bonds, the inductive effect of the two C—Cl dipoles in the phosgene molecule upon the C=O

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[3] Atkinson, Heycock and Pope, *J. Chem. Soc.*, **117**, 1410 (1920).

[4] "Organic Syntheses," John Wiley and Sons, Inc., New York, 1932, Collective Vol. I, p. 307.

[5] Smyth, THIS JOURNAL, **51**, 2051 (1929); *J. Chem. Phys.*, **1**, 247 (1933).

[6] Dornte, THIS JOURNAL, **55**, 4126 (1933).

[7] *Cf.* Smyth, *Phil. Mag.*, **50**, 361 (1925).

group should be not far from that of the two C—Cl dipoles in methylene chloride upon the two C—H bonds. The acetone moment,[8,9] 2.85 × $10^{-18}$, minus the methylene chloride moment,[10] 1.57 × $10^{-18}$, gives a difference, 1.28 × $10^{-18}$, as compared to the moment, 1.18 × $10^{-18}$, observed for the phosgene molecule. A factor not considered in this calculation is the larger Cl–C–Cl angle 124° in the methylene chloride molecule found by Bewilogua in x-ray diffraction investigations.[11] The reduction of this angle to 110° in the phosgene molecule should increase the resultant of the two C–Cl dipoles to a value somewhat less than $1.57 \times 10^{-18} \cos 55°/\cos 62° = 1.92 \times 10^{-18}$. This value is too high, as it does not take into account the reduction of the C–Cl moments by the increase in induction due to the alteration in their positions. Subtraction of this value from the acetone moment gives 0.93 × $10^{-18}$ for the phosgene moment. Aside from the neglected increase in the inductive effect between the two C–Cl moments which makes this calculated value too low, the probable errors in the experimental values for the valence angles are sufficiently large to permit of this difference between the observed and the calculated moment of $COCl_2$.

In the acetyl chloride molecule, as in the phosgene molecule, it seems approximately correct to assign a moment equal to that of acetone, 2.85 × $10^{-18}$, to the direction of the C=O bond. In view of the polarizabilities of the C=O and C—C bonds, a moment equal to that of methyl chloride,[12] 1.86 × $10^{-18}$, is assigned to the C—Cl direction. Dornte's[6] electron diffraction investigations give the value 110 ± 10° for the C–C–Cl angle, which if the valences are symmetrical, makes the angle between the C=O and the C—Cl directions 125 ± 10°. When the two moments are resolved with this angle between them, 2.35 × $10^{-18}$ is obtained as the resultant as compared to the observed[9] 2.68 × $10^{-18}$. Lowering of the moment in the C—Cl direction to as little as 1.0 × $10^{-18}$ raises the calculated resultant only to 2.42 × $10^{-81}$. As there is no reason for raising the moment in the C=O direction above 2.85 × $10^{-18}$, the cause of the discrepancy may best be sought in the valence angle. With the component moments, 2.85 and 1.86 × $10^{-18}$, lowering of the Cl—C=O angle to 114.5°, a change just at the limit of the probable error of the electron diffraction experiment, gives a resultant equal to the observed moment of acetyl chloride. Although there is no other evidence for such a distortion of this valence angle, it may be noted that it is smaller than the distortion of the C–C–Cl angle in methylene chloride.

The moment found for hydrogen cyanide is much larger than the value 2.1 × $10^{-18}$ obtained by Fredenhagen and Maske,[13] and, in view of close conformity of the polarization values to the $P$–$1/T$ line, is considered very accurate. There is a sharp rise from this value 2.93 for HCN to the value 3.45 for $CH_3CN$ found by Snoek[14] from measurements in solution. This latter value is presumably to be accepted as replacing the earlier value 3.11 determined by Werner.[15] The increase in moment resulting from the replacement of hydrogen by methyl is somewhat less than in the case of the hydrogen halides and is relatively considerably less.

As the hydrogen or the methyl carbon lies at least approximately in the extension of the line joining the cyanide carbon and nitrogen nuclei,[16,17] methyl cyanide and the chloromethyl cyanides measured by Snoek may be examined just as were the halogenated methanes in earlier work.[1] The moment calculated for $CH_2ClCN$ by assigning the moment of $CH_3Cl$, 1.86, to the C—Cl line and that of $CH_3CN$, 3.45, to the C–CN line and assuming an angle of 110° between them is 3.31 as compared to 2.97 × $10^{-18}$ observed by Snoek. This assignment to the bonds of the moments of the methyl compounds is an approximation, which also takes account of the effects of the C—H moments, permanent or induced.[1] A widening of the angle between the C–Cl and the C–CN lines to 124° as in the case of methylene chloride would lower the calculated moment to 2.86 × $10^{-18}$. However, in view of the lowering of adjacent moments by mutual inductance previously calculated and observed,[1] it is probable that the lowering of the observed moment as compared to that calculated on the basis of a 110° valence angle is due to inductive effect. The moment of $CCl_3CN$ should be approximately equal to the difference between

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[8] Stuart, *Z. Physik*, **50**, 490 (1928).

[9] Zahn, *Physik. Z.*, **33**, 686 (1932).

[10] Sänger, *ibid.*, **27**, 556 (1926).

[11] Bewilogua, *ibid.*, **31**, 265 (1930).

[12] Sänger, *Helv. Phys. Acta*, **3**, 161 (1930); *Physik. Z.*, **32**, 20 (1931); Fuchs, *Z. Physik*, **63**, 824 (1930).

[13] Fredenhagen and Maske, *Z. physik. Chem.*, **B10**, 142 (1930).

[14] Snoek, *Physik. Z.*, **35**, 196 (1934).

[15] Werner, *Z. physik. Chem.*, **B4**, 371 (1929).

[16] Pauling, THIS JOURNAL, **53**, 1367 (1931).

[17] Smyth and Walls, *ibid.*, **54**, 1854 (1932).

that of HCN and that of $CHCl_3$, $2.93 - 1.05 = 1.88$, or the difference between $CH_3CN$ and $CH_3CCl_3$,[18] $3.45 - 1.5 = 1.95$. The value $2.0 \times 10^{-18}$ observed by Snoek differs from the calculated values by less than the experimental error.

In the nitromethanes, the moment of the nitro group should act in the C—N line[17] and the moment relations should resemble those in the methyl cyanides. The moment $3.42 \times 10^{-18}$ found for nitromethane is considerably lower than the approximate value $3.78 \times 10^{-18}$ calculated by Höjendahl[19] from the measurements of Pohrt on the vapor and higher than the values 3.04,[20] 3.05[19] and 3.13[21] found in solution. The moment of $CCl_3NO_2$ should be approximately equal to the difference between that of $CH_3NO_2$ and that of $CH_3CCl_3$, $3.42 - 1.5 = 1.92$, which is in excellent agreement with the value 1.88 in Table II.

In spite of the fact that the dipoles of the carbonyl, nitro and cyanide groups are larger than those which have previously been examined in such close proximity to one another, there is no evidence of any exceptionally large induced shift of charge or alteration of valence angle in the molecules. In these aliphatic molecules, any shifts of charge other than those due to simple inductive effect are too small to be detected.

## Summary

The dielectric constants of the vapors of phosgene, hydrogen cyanide, nitromethane and chloropicrin have been measured and used to calculate the dipole moments of the molecules of these substances. The values thus obtained, together with the moments of other similar molecules, are found to conform closely to the moments calculated on the assumption of a central tetrahedral carbon atom.

PRINCETON, NEW JERSEY RECEIVED JUNE 14, 1934

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[18] Van Arkel and Snoek, *Z. physik. Chem.*, **B18**, 159 (1932).

[19] Höjendahl, "Thesis," Copenhagen, 1928; *Physik. Z.*, **30**, 391 (1929).

[20] Hunter and Partington, *J. Chem. Soc.*, 312 (1932).

[21] Weissberger and Sängewald, *Ber.*, **65**, 701 (1932).

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF UPSALA]

# The Molecular Weight of Erythrocruorin. II.

BY THE SVEDBERG AND INGA-BRITTA ERIKSSON-QUENSEL

In a previous communication[1] a report has been given of the determination by centrifugal methods of the molecular weight, the sedimentation constant and the PH stability range of the red proteins dissolved in the blood of the lugworm, *Arenicola marina* and the earthworm, *Lumbricus terrestris*. Both with regard to molecular mass and electrochemical properties such marked differences were found between the respiratory pigments in question on the one hand and the hemoglobin of the vertebrates on the other that it was proposed to revive the name erythrocruorin formerly used by Ray Lankester for the red blood proteins of the invertebrates. The sedimentation constant of *Arenicola* erythrocruorin is $57.4 \times 10^{-13}$, that of *Lumbricus* erythrocruorin $60.9 \times 10^{-13}$. By means of a mixture test it could be proved that the difference between the two constants expressed by the above values is real. The molecular weight was found to be around 2,800,000 in both cases. The experimental error in the sedimentation constant is probably less than 1%. The molecular weight, however, being determined by means of the sedimentation equilibrium method, which is difficult to handle in case of very heavy molecules, may be in error to an extent of about 10%.[1a]

In the course of a comparative study of the respiratory proteins throughout the animal kingdom, Mrs. Astrid Hedenius discovered several other varieties of erythrocruorin characterized by different sedimentation constants.[2] It seemed to us desirable to determine the PH stability range and the molecular weight for at least one representative of each of these new types of erythrocruorin.

At the present time ten different sedimentation constants are known from the red blood pigments, *viz.*, 60.9, 57.4, 33.7, (22.4), 16.3, (11.6), (7.1), 4.4, 3.5, $1.9 \times 10^{-13}$. Erythrocruorin characterized by the two first constants was

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[1] Svedberg and Eriksson, THIS JOURNAL, **55**, 2834 (1933).

[1a] Recent determinations by means of a more accurate method of observation have given a slightly higher value, *viz.*, 3,200,000.

[2] Svedberg and Hedenius, *Nature*, **131**, 325 (1933); *J. Biol. Chem.*, **103**, 311 (1933); Biological Bulletin, **66**, 191 (1934).