anhydrous hydrogen bromide (Dow Chemical Co.) at 110–115° to constant weight. After separation of the aqueous layer the organic material was chilled to 2°, washed with two ice-cold portions of concentrated sulfuric acid, 3% ammonia water, twice with water, and dried over anhydrous calcium chloride followed by anhydrous potassium carbonate. Fractional distillation[12a] gave the purified bromide, b.p. 111° (96 mm.), $n^{20}D$ 1.4500, in 85% yield.

**Benzyl Chloride.**—Fractional distillation[12a] of Eastman Kodak Co. White Label benzyl chloride yielded pure material: b.p. 124° (150 mm.), $n^{20}D$ 1.5386.

The Grignard reagent prepared in 2500 ml. of anhydrous ether from 121.5 g. (5 g. atoms) of magnesium and 860 g. (4.8 moles) of *n*-heptyl bromide was filtered from the excess magnesium. After standing 84 hours the Grignard reagent was pumped away from the sludge. It was heated to reflux (42°), and 554 g. (4.38 moles) of benzyl chloride added over a period of one hour. The reaction was continued for 44 hours, removing aliquots intermittently for analysis. The analytical data are shown in Table II. The product was hydrolyzed on ice and the organic material separated by ether extraction. After removal of the ether, fractionation[12b] of the organic material led to the isolation of an unidentified low boiling material: 35.7 g., b.p. 51–52.5°, $n^{20}D$ 1.3604–1.3929; 280.3 g. of heptane and heptene; 42.6 g. of unreacted benzyl chloride; 41.4 g. of a complex high boiling material and a 286.5 g. of residue. Refractionation[13] of the heptane–heptene mixture yielded 109 g. (1.11 moles) of 1-heptene, b.p. 92.0–92.7°, $n^{20}D$ 1.3989–1.3998 and 168 g. (1.68 moles) of *n*-heptane, b.p. 97.0–97.3°, $n^{20}D$ 1.3877–3882. The hydrocarbons were identified by comparing their properties with those of the pure materials. The benzyl chloride fractions (50.9 g.) contained 42.6 g. (0.34 mole) of the halide as determined by the hydrolysis procedure.[14] An anilide prepared from the benzyl chloride had a m.p. 115–116°, mixed m.p. 114–115°. The residue was chilled to −5° to give 186 g. (1.02 moles) of bibenzyl, which after recrystallization from ether melted at 51–52°, mixed m.p. 51–52°. The liquid residue plus the high boiling fractions above were distilled through a high vacuum column,[15] at 1 mm. The following products were identified: an additional 21.8 g. (0.12 mole) bibenzyl; 2.0 g. of tetradecane, m.p. 5.5–6.5°, mixed m.p. 6.0–6.5°; 10 g. (0.04 mole) benzylphenylethylbenzene, mol. wt. calcd. 273, found 265, mol. ref. calcd. 88.5, found 86.7, $n^{20}D$ 1.5929,[7] found 1.5941. A few fractions (5.2 g.), which were suspected to contain 1-phenyloctane, were selectively adsorbed on silica gel. Two-tenths gram of material was obtained which is believed to be 1-phenyloctane; $n^{20}D$ 1.4847,[16] found 1.4846–1.4850, m.p.[16] −37.0°, found −43 to −36°. The bulk of the fractions could not be identified but from their properties appeared to be mixtures of polyaromatics.

TABLE II

| Sample | Time, hr. | Temp., °C. | Moles of Grignard | Moles of $C_6H_5CH_2Cl$ |
|---|---|---|---|---|
| 1 | 0 | 20 | 4.38 | 0.0 |
| 2 | 1.25 | 42 | 3.42 | 3.13 |
| 3 | 1.75 | 41 | 2.86 | 2.54 |
| 4 | 2.5 | 41 | 2.43 | 2.29 |
| 5 | 3 | 42 | 2.11 | 1.95 |
| 6 | 4.5 | 41.5 | 1.39 | 1.39 |
| 7 | 5.25 | 41.5 | 1.18 | 1.15 |
| 8 | 7.5 | 38 | 0.76 | 0.70 |
| 9 | 9 | 36 | .69 | .. |
| 10 | 13.75 | 33 | .55 | .53 |
| 11 | 20 | 32 | .45 | .45 |
| 12 | 44 | 28 | .37 | .33 |

**Analysis of the $C_6H_5CH_2Cl$–RMgX Mixtures.**—*n*-Heptylmagnesium bromide was determined using a procedure similar to Gilman's[17] except that the heating operation was avoided. After the addition of the sample to 50 ml. of cold distilled water, a measured excess of standard acid was added. The mixture was allowed to stand for one-half hour at 25° and then the acid neutralized with standard base. This titration yielded the amount of RMgX present. The method of estimating benzyl chloride in the presence of *n*-heptylmagnesium bromide depends on the difference in the rate of hydrolysis of the two compounds.

After the Grignard titration, the benzyl chloride was determined by adding 50 ml. of 0.2 *N* NaOH and making the solution up to a volume of about 150 ml. To the alkaline solution was added 60 ml. of 95% ethanol; thus the solution was approximately 0.045 *N* NaOH in 27% ethanol. Hydrolyses were carried out at the reflux temperature of the mixture for one-half hour. After cooling, excess alkali was titrated with standard acid. A blank determination was run. Analyses of synthetic mixtures indicated an accuracy of ±2% and infrared analyses of two mixtures for benzyl chloride agreed within ±2% of the titration values.

**Acknowledgment.**—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

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(13) The column was of the total condensation, partial take-off type packed with $^3/_{64}''$ stainless steel helices. The column, with a packed section 1.1 × 75 cm., had 80 theoretical plates.

(14) The fractions had amounts of benzyl chloride varying from 33–100%. Qualitative tests showed no halogen present but chlorine; however analysis for total halogen indicated that some additional chlorine-containing compound was present in these fractions. This could not be identified and amounted to approximately 4 g.

(15) Nine to ten theoretical plates. To be described in a separate publication to be submitted to *Analytical Chemistry*.

(16) Schiessler, *et al.*, *Proc. A.P.I.*, **26** (III), 254–302 (1946).

(17) Gilman and Meyers, THIS JOURNAL, **45**, 159 (1923).

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## Dehalogenation of 2-Amino-4-methyl-6-chloropyrimidine

BY D. SHAPIRO

Hydrogen is evolved vigorously from an alcoholic or aqueous solution of ammonium chloride, when heated with zinc in presence of Raney nickel. It appears that Raney nickel catalyzes the otherwise sluggish[1,2] reaction

$$2NH_4Cl + Zn \longrightarrow ZnCl_2 + 2NH_3 + H_2$$

Part of the ammonia, liberated according to this equation, accompanies the hydrogen; part is bound by the zinc salt.

The above system was found to dehalogenate smoothly 2-amino-4-methyl-6-chloropyrimidine to the 2-amino-4-methyl compound which is an intermediate in the synthesis of sulfamerazine.[3]

A solution of 20 g. of 2-amino-4-methyl-6-chloropyrimidine[4] in a mixture of 16 cc. of concentrated hydrochloric acid and 250 cc. of water (40–50°) was neutralized with a solution of 7 g. of sodium hydroxide in 100 cc. of water, with vigorous stirring; the temperature was raised to 70–75°, and 20 g. of ammonium chloride and 1.5 g. of Raney nickel added. Over a period of 90 minutes, 40 g. of zinc dust was introduced, causing a lively effervescence of the mass. (Occasionally, it was found advisable to add another 2 g. of Raney nickel to the mixture.) Stirring and heating were continued for one more hour and, after addition of a solution of 26 g. of sodium hydroxide in 80 cc. of water, for 30 more minutes and at 90–95°. The solid was removed by filtration, washed with hot water, and the filtrate evaporated *in vacuo* to a volume of about 200 cc. At boiling temperature, 100 cc. of 30% sodium hydroxide solution was added. After 12 hours, the crystals of 2-amino-4-methyl-pyrimidine were filtered and dissolved in boiling acetone. The filtered solution, upon concentration, gave 12 g. (80%) of product of correct m.p. 159–161°. The method is quicker

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(1) Ritthausen, *J. prakt. Chem.*, **60**, 473 (1893).

(2) Drucker, *Z. Elektrochem.*, **29**, 412 (1923).

(3) Roblin, *et al.*, THIS JOURNAL, **62**, 2002 (1940).

(4) Gabriel and Coleman, *Ber.*, **32**, 2921 (1899).

and more reliable than the reduction with zinc dust and water, described by Gabriel and Coleman.[4]

An attempt was also made to reduce 4-methyl-2,6-dichloropurine[5] by the same method. According to E. Fischer,[6] however, the expected 7-methyl-2-chloropurine is not stable in contact with dilute alkali, but is converted into 7-methyl-2-hydroxypurine (m.p. 323°) and an unidentified substance of the composition $C_5H_7ClN_4$ (m.p. 251°). Indeed, two substances of these melting points, respectively, were isolated, when the reaction product was worked up.

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(5) E. Fischer, *ibid.*, **30**, 2400 (1897).

(6) E. Fischer, *ibid.*, **31**, 2550 (1898).

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## Integral Diffusion Coefficients of Potassium Chloride Solutions for Calibration of Diaphragm Cells

BY R. H. STOKES

Gosting[1] has recently obtained absolute measurements of the differential diffusion coefficients of potassium chloride in water at 25° from 0.1 *N* to 3.9 *N* by the Goüy interference technique. Harned and Nuttall,[2] using a conductimetric method, have also obtained absolute values in the range 0.00125 *N* to 0.5 *N*, which are in extraordinarily good agreement with those of Gosting in the overlapping part of the range. Thus the combined data may be used with complete confidence for testing and calibrating other types of diffusion apparatus. For diaphragm-cell measurements, however, it is convenient to start the diffusion with solution on one side of the diaphragm and pure water on the other,[3] in which case the diffusion coefficient obtained is a rather complicated average value, $\bar{D}$, called the "diaphragm-cell integral coefficient."

Under these conditions, denoting the mean of the initial and final concentrations on the solution side by $c_m'$, and the mean concentration on the other side by $c_m''$ (which is half the final concentration on the side which was initially pure water), it has been shown[3] that

$$\bar{D}^0_{(c_m')} = \bar{D} - \frac{c_m''}{c_m'}\left[\bar{D} - \bar{D}^0_{(c_m'')}\right] \qquad (1a)$$

or

$$\bar{D} = \left[\bar{D}^0_{(c_m')} - \frac{c_m''}{c_m'}\bar{D}^0_{(c_m'')}\right] \Big/ \left(1 - \frac{c_m''}{c_m'}\right) \qquad (1b)$$

Here the quantity $\bar{D}^0_{(c)}$ is the "integral diffusion coefficient for a run of vanishingly short duration" between the concentration *c* and pure water, given by

$$\bar{D}^0_{(c)} = \frac{1}{c}\int_0^c D\,dc \qquad (2)$$

*D* being the true differential diffusion coefficient as measured for example by the optical or conductimetric methods. It is consequently very useful in diaphragm-cell work to have a table of values of the quantity $\bar{D}^0_{(c)}$ for all values of *c* for the calibration solution, as it is then unnecessary to select a particular length of run or initial concentration of the calibration solution, and the cell may readily be checked for constancy of "cell constant" over a range of concentration. Table I provides these data, obtained by tabular and graphical integration of the results of Gosting and of Harned and Nuttall according to equation (2).

TABLE I

INTEGRAL DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE SOLUTIONS AT 25°

$\bar{D}^0 = \frac{1}{c}\int_0^c D\,dc$. (*c* in moles/liter, $\bar{D}^0$ in cm.$^2$ sec$^{-1}$ × $10^{-5}$)

| $c$ | $\bar{D}^0$ | $c$ | $\bar{D}^0$ | $c$ | $\bar{D}^0$ |
|---|---|---|---|---|---|
| 0.000 | 1.996 | 0.05 | 1.893 | 1.4 | 1.874 |
| .001 | 1.974 | .07 | 1.883 | 1.6 | 1.882 |
| .002 | 1.966 | .1 | 1.873 | 1.8 | 1.892 |
| .003 | 1.960 | .2 | 1.857 | 2.0 | 1.901 |
| .005 | 1.951 | .3 | 1.850 | 2.5 | 1.927 |
| .007 | 1.945 | .5 | 1.848 | 3.0 | 1.953 |
| .01 | 1.938 | .7 | 1.851 | 3.5 | 1.979 |
| .02 | 1.920 | 1.0 | 1.859 | 3.9 | 2.000 |
| .03 | 1.908 | 1.2 | 1.866 | | |

TABLE II

FURTHER DIAPHRAGM CELL MEASUREMENTS ON POTASSIUM CHLORIDE SOLUTIONS AT 25°

$c_m'$ in moles/liter, $\bar{D}^0_{c_m'}$ in cm.$^2$ sec.$^{-1}$ × $10^{-5}$

| $c_m'$ | $\bar{D}^0_{c_m'}$ | $c_m'$ | $\bar{D}^0_{c_m'}$ |
|---|---|---|---|
| 0.3877 | 1.853 | 0.8721 | 1.854 |
| .3911 | 1.849 | .8344 | 1.854 |
| .6310 | 1.842 | .8820 | 1.851 |
| .6188 | 1.851 | .8972 | 1.852 |
| .6462 | 1.851 | | |

In the figure, the data of Table I are compared graphically with the diaphragm-cell results previously reported by the writer.[3] (The open circles on this graph represent the means of each pair of approximately duplicate runs reported in Table III of reference (3).) It is clear that, though the average deviation of the points from the standard curve is less than 0.3%, most of this deviation is due to the points near the minimum. As the measurements represented by these points hap-

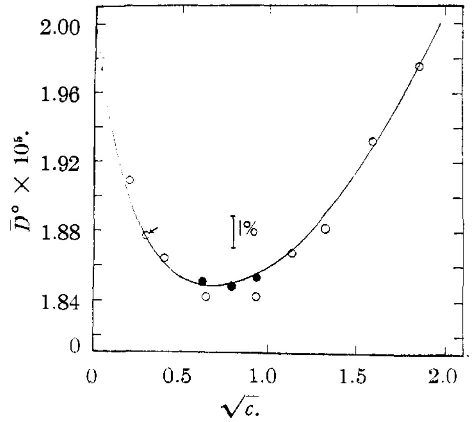

Fig. 1.—Integral diffusion coefficients of potassium chloride at 25°: full curve, calculated from differential values of Gosting, Harned and Nuttall (Table I); open circles, original diaphragm-cell measurements (reference 3); filled circles, new measurements (Table II); arrow, calibration point for diaphragm-cells.

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(1) L. J. Gosting, THIS JOURNAL, **72**, 4418 (1950).

(2) H. S. Harned and R. L. Nuttall, *ibid.*, **69**, 736 (1947); **71**, 1460 (1949).

(3) R. H. Stokes, *ibid.*, **72**, 763, 2243 (1950).