MacInnes and Belcher's values agree somewhat more closely but not really satisfactorily. However, in spite of these differences, these conductance and electromotive force values are in much better agreement than the earlier values[13] which range between far greater limits. The heat content data check fairly well when we take into account that they were derived by differentiation. Direct calorimetric measurements have been made recently by Pitzer[14] who reported $\Delta H_i^0 = 1843 \pm 60$ cal. at 25°.

Summary

1. The solubility of carbon dioxide in water and aqueous sodium chloride solutions from 0 to 50° has been measured by analyzing the solution contained in cells which were employed for the electromotive force measurements and with the conditions identical in both cases.

2. The logarithms of the Henry's law constants computed from these measurements were expressed by quadratic equations and the constants for these equations were found by the method of least squares.

3. The first dissociation constant of carbonic acid from 0 to 50° was measured by means of cells without liquid junction.

4. The logarithms of the dissociation constants were expressed by a least squared equation. The thermodynamic quantities for the dissociation were calculated from this equation.

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[13] Kauko and Elo, *Z. physik. Chem.*, **A184**, 211 (1939), for example, obtained 2.33×10^{-7} and 3.46×10^{-7} at 0° and 25°, respectively.

[14] Pitzer, THIS JOURNAL, **59**, 2365 (1937).

NOTES

Derivatives of 2-Bromo-3-methylpentanoic Acid

BY CHARLES D. HURD AND F. W. CASHION

In the course of another investigation, 2-bromo-3-methylpentanoyl bromide and several of its derivatives have been prepared.

To a mixture of 25 g. of 3-methylpentanoic acid[1] with 3 g. of red phosphorus in a 200-cc. three-neck flask fitted with a condenser, mercury seal stirrer, and separatory funnel, 30 g. of bromine was added slowly with stirring. The flask was then placed on a water-bath at 95° and about 30 g. of bromine added with stirring until no further absorption took place. The product was distilled at 23 mm. pressure and the fraction boiling between 92 and 102° collected. Redistilled, a yield of 30 g., or 54% of colorless 2-bromo-3-methylpentanoyl bromide, boiling at 98–100° under 23 mm. pressure and fuming in air, was obtained. It was analyzed for bromine by fusion with sodium peroxide.

Anal. Calcd. for $C_6H_{10}OBr_2$: Br, 62.0. Found: Br, 63.1.

2-Bromo-3-methylpentanamide.—A well-stirred mixture of 1 g. of the acid bromide in 10 cc. of concentrated ammonium hydroxide was filtered and the solid amide crystallized from 2 cc. of a 25% aqueous alcohol; yield, 0.3 g. of a white crystalline substance, m. p. 104° and slightly soluble in water.

Anal. Calcd. for $C_6H_{12}ONBr$: Br, 41.2. Found: Br, 40.7.

2-Bromo-3-methylpentananilide.—One gram of the acid bromide was mixed with 1 g. of aniline. Considerable heat was evolved. After trituration with 10 cc. of water and decantation, the remaining solid was crystallized twice from 4-cc. portions of a 60% aqueous alcohol; yield, 0.5 g. of a white, crystalline, water-soluble compound of m. p. 84°.

Anal. Calcd. for $C_{12}H_{16}ONBr$: Br, 29.6. Found: Br, 30.3.

2-Bromo-3-methylpentane-*p*-toluidide.—A similar procedure to the above with 1 g. of *p*-toluidine yielded 0.6 g. of the white, water-insoluble *p*-toluidide, m. p. 105°.

Anal. Calcd. for $C_{13}H_{18}ONBr$: Br, 28.1. Found: Br, 28.8.

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[1] "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1931, Vol. 11, p. 76.

2,2,2-Trifluoroethyl Iodide

BY HENRY GILMAN AND R. G. JONES

2,2,2-Trifluoroethyl iodide has been prepared by the reaction of hydrogen iodide with 2,2,2-trifluorodiazoethane[1a] in toluene solution at −75°. Although the reaction was violent at the low temperature used, a 77% yield of trifluoroethyl iodide was obtained.

$$CF_3CHN_2 + HI \longrightarrow CF_3CH_2I + N_2$$

The reaction of red phosphorus and iodine with trifluoroethanol[1b] produced large quantities of hydrogen iodide, but gave only very small yields of the 2,2,2-trifluoroethyl iodide.

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[1] (a) Gilman and Jones, THIS JOURNAL, **65**, 1458 (1943); (b) Gilman and Jones, *ibid.*, **65**, (1943).

Trifluoroethyl iodide reacted readily with magnesium, but no Grignard reagent was obtained. Instead, the iodine atom and one fluorine atom were extracted, and 1,1-difluoroethylene was formed. Henne[2] has noted a similar reaction

$$CF_3CH_2I + Mg \longrightarrow CF_2{=}CH_2 + MgIF$$

between 2,2-difluoroethyl iodide and magnesium, sodium, or potassium, the organic product being fluoroethylene.

These reactions illustrate the difficulty of preparing a Grignard reagent from a 1,2-dihalogen compound. It is possible that trifluoroethyllithium can be prepared by a halogen–metal interconversion reaction[3] using ethyllithium at low temperatures.

Experimental

2,2,2-Trifluoroethyl Iodide.—Free trifluorodiazoethane was prepared as described previously.[1a] A solution made by dissolving 12.7 g. (0.115 mole) of the diazo compound in 25 cc. of toluene at −75°, was gently stirred, and to it was added dropwise a solution of 15 g. (0.117 mole) of pure hydrogen iodide in 25 cc. of toluene also cooled to −75°. The addition of the hydrogen iodide solution was conveniently made by means of a small pipet to which was attached a rubber bulb for filling. The reaction was violent even at −75°, and the mixture was soon colored with free iodine. This iodine color persisted after all of the hydrogen iodide solution had been added and the mixture had stood in the "dry-ice"–acetone bath for twelve hours. However, when the reaction mixture was allowed to warm up to room temperature, the iodine color quickly faded, and this indicated that some unreacted trifluorodiazoethane was still present. The mixture was therefore cooled again to −75° and treated with another 2 g. of hydrogen iodide dissolved in 5 cc. of toluene.

The reaction mixture was distilled through a small packed column and the first fraction, boiling from 50 to 105°, was collected. This fraction was redistilled through the same column to yield 16.0 g. of pure 2,2,2-trifluoroethyl iodide, b. p. 54.5–55° (730 mm.); d^{23}_4 1.989.

Anal. Calcd. for CF_3CH_2I: I, 60.46. Found: I, 60.15, 60.52.

An additional 2.5 g. of liquid was obtained which boiled from 55 to 57°, and this was probably slightly impure trifluoroethyl iodide. This made a total yield of 18.5 g. (77%). The compound is a colorless liquid with an odor similar to ethyl iodide or bromide.

Action of Phosphorus and Iodine on Trifluoroethanol.—A mixture of 48 g. (0.48 mole) of 2,2,2-trifluoroethanol[1b] and 8 g. (0.26 atom) of dry red phosphorus was placed in a 100-cc. flask carrying an efficient reflux condenser. Dry powdered iodine (65 g., 0.5 atom) was added through the condenser in small portions while the flask was kept in a water-bath at 75°. After all of the iodine had been added, the mixture was refluxed for one and a half hours. Hydrogen iodide was copiously evolved. The reaction mixture was distilled, and a white, porous, solid residue remained. The distillate was shaken with 100 cc. of water, and the heavy non-aqueous layer (12 g.) was separated and dried over potassium carbonate. Upon distillation of this liquid, 5.1 g. (5%) of crude trifluoroethyl iodide was obtained (b. p. 55–58°). The aqueous solution was extracted with three 30-cc. portions of ether. This extract was washed with sodium thiosulfate solution, dried over calcium chloride, and fractionated to yield 19 g. (40%) of unchanged trifluoroethanol.

The white solid residue in the original reaction flask was treated with 50 cc. of water, and the mixture was distilled by heating with an open flame. Five grams of unreacted phosphorus remained. The distillate, consisting of two liquid phases, was extracted with 25 cc. of ether. After drying this extract and removing the ether, the residual liquid (8 g.) boiled at 181–183°. It has not been identified.

In another experiment a mixture of 20 g. (0.20 mole) of trifluoroethanol, 6.2 g. (0.20 atom) of phosphorus, and 127 g. (1.0 atom) of iodine was heated at 50° for four hours, 75° for two hours, 100° for a few minutes. Large quantities of hydrogen iodide were evolved. From this reaction were isolated 1.8 g. (4% yield) of crude trifluoroethyl iodide; 5 g. (25%) of unchanged trifluoroethanol; and 10 g. of a white wax-like solid which has not been identified.

Reaction of Trifluoroethyl Iodide with Magnesium.—A 100-cc. three-necked flask, provided with a mechanical stirrer, dropping funnel, and reflux condenser, was thoroughly dried and swept out with nitrogen. In the flask was placed 1.50 g. (0.062 atom) of fine magnesium turnings, 15 cc. of dry ether, and 1.0 g. (0.008 atom) of iodine. When all of the iodine had reacted, a solution of 10.5 g. (0.050 mole) of pure trifluoroethyl iodide in 20 cc. of dry ether was added dropwise to the well-stirred mixture in the flask. Reaction took place immediately, and gas was evolved which was collected over water. As soon as all of the trifluoroethyl iodide had been added the gas evolution stopped. A color test[4] with Michler ketone on a 1-cc. portion of the reaction mixture was negative. This indicated that no Grignard reagent was present. Analysis was made on an aliquot portion of the gas which was found to contain 0.045 mole of an ethylenic compound. The remainder of the gas was bubbled very slowly into 8 g. of bromine which absorbed all but a small portion. Upon distillation of the reaction product, 7.0 g. of colorless liquid was obtained which had the following constants: b. p. 91° (740 mm.), d^{27}_4 2.141. Swarts[5] has described the reaction of 1,1-difluoroethylene with bromine to yield 1,1-difluoro-1,2-dibromoethane, b. p. 93°, d^{12}_4 2.242. The ethylenic gas was therefore assumed to be 1,1-difluoroethylene, and the yield was 90%.

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[2] Henne, This Journal, **60**, 2275 (1938).

[3] Gilman and Jones, *ibid.*, **63**, 1441 (1941).

[4] Gilman and Schulze, *ibid.*, **47**, 2002 (1925).

[5] Swarts, *Bull. Acad. Roy. Belg.*, 383 (1901).

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A Note on 10-Iodohydroquinines

BY ALICE G. RENFREW, C. L. BUTLER AND L. H. CRETCHER

The addition of hydrogen iodide to β-isoquinine is reported below. Saturation of the semi-cyclic