NOTES

Molar Heats of Solution of *n*-Butylboric Acid and Tri-*n*-butylboric Oxide[1]

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n-Butylboric acid (*n*-butane boronic acid) and its anhydride, tri-*n*-butylboric oxide, form an interesting pair of compounds. At room temperature the acid is a solid, while the oxide is a liquid. One is confronted with the unusual circumstance of having a liquid anhydride which reacts with water to produce the solid acid. In our program of study of the thermochemistry of boron compounds we determined the heats of solution of both *n*-butylboric acid and tri-*n*-butylboric oxide with the intention of also determining their heats of formation. Since it appears that this latter objective will be postponed indefinitely we are reporting the heat of solution data at this time.

Experimental.—A description of the heat of solution calorimeter and details of its operation and calibration have been given by us in a previous publication.[3] As before the calorimeter contained 520.0 (±0.1) g. of water in all experiments and its heat capacity when filled was 568.4 ± 1.2 cal./deg.

n-Butylboric acid and tri-*n*-butylboric oxide were prepared and kindly supplied to us by Dr. Charles Ericson of this Laboratory who used the method of Mattraw.[4] Analyses showed the samples to be pure, though the difficulty of boron analysis with this type of compound results in precision no greater than about 1%. Impurities which might have been present in quite small amounts would have had structure and properties similar to the compounds under study.

Results and Discussion.—Tri-*n*-butylboric oxide hydrolyzes to yield *n*-butylboric acid according to the equation

$$(C_4H_9BO)_3 + 3H_2O + Aq = 3C_4H_9B(OH)_2{\cdot}Aq \quad (1)$$

A series of five determinations of the heat of this hydrolysis yielded an average of $\Delta H = -11.6 \pm 0.15$ kcal./mole of $(C_4H_9BO_3)_3$ when the average concentration of the *n*-butylboric acid produced was 0.024 *m*. The actual range of concentration varied from about 0.05 to 0.007 *m* and although there was a hint of slight decrease of heat of hydrolysis with increasing concentration, such dependence, if it exists in the concentration range studied, lies within the accuracy of the measurements. Difficulties were introduced in these measurements by the low solubility and slow rate of dissolution of *n*-butylboric acid which tended to stick to stirrer and sample tubes when produced in the calorimeter according to reaction 1.

Five measurements of the heat of solution of small samples of *n*-butylboric acid yielded an average heat of solution of $\Delta H = 2.67 \pm 0.06$ kcal./mole when the average concentration of the acid was 0.008 *m*, with the actual concentrations ranging between 0.006 and 0.009 *m*. No trend was observed in the results. The accuracy of the measurements was low (±2.3%) because of use of quite small samples necessitated by a very limited supply of the compound.

From the experimental data, assuming no concentration dependence, one calculates that the heat of conversion of the liquid oxide to crystalline acid is exothermic 19.6 kcal./mole of oxide (per 3 moles of acid).

The results may be summarized by the following equations

$$(1) \quad (C_4H_9BO)_3(l) + 3H_2O + Aq \longrightarrow 3C_4H_9B(OH)_2{\cdot}Aq \quad \Delta H = -11.6 \pm 0.2$$

$$(2) \quad C_4H_9B(OH)_2(c) + Aq \longrightarrow C_4H_9B(OH)_2{\cdot}Aq \quad \Delta H = 2.7 \pm 0.1$$

$$(3) \quad (C_4H_9BO)_3(l) + 3H_2O \longrightarrow 3C_4H_9B(OH)_2(c) \quad \Delta H = -19.6 \pm 0.4$$

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[1] In part from the M.S. thesis of A. S. Dworkin, Cornell University, September, 1951.

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[3] E. R. Van Artsdalen and A. S. Dworkin, This Journal, **74**, 3401 (1952).

[4] H. C. Mattraw, Thesis, Cornell University, 1950.

Electric Moments from Extrapolated Mixed Solvent Data

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Many compounds have insufficient solubility in non-polar, non-donor type solvents (such as benzene) to permit determinations of electric moments by the dilute solution method. In many such cases moments have been determined in 1,4-dioxane solution, but the values obtained are generally too high due to solute–solvent hydrogen bonding effects.

Preliminary results of a method intended for the determination of benzene solution moments for compounds not soluble in benzene, through extrapolation to pure benzene of mixed solvent data, are reported here.

A benzene-soluble compound of intermediate moment and exhibiting considerable solvent effect in dioxane solution (*p*-chloroaniline: μ 2.99 benz.; 3.36 diox.)[1] was chosen for the first investigation.

Dielectric constant data were determined as indicated in Fig. 1.

The lines show the variation of dielectric constant of equimolar solutions as a function of mixed solvent environment. The zero molarity line is for pure mixed solvent.

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[1] C. Curran and G. K. Estok, This Journal, **72**, 4575 (1950).