NOTES

Concerning Edmonds and Birnbaum's Equation for the Equilibrium Constant for the Formation of a Colored Complex[1]

By Edward S. Amis

Edmonds and Birnbaum[2] from

$$\frac{y}{x} = \frac{\log I_y}{\log I_x} \tag{1}$$

obtained the equation

$$K = \frac{b^n d^n(\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y} \tag{2}$$

for the equilibrium constant, K, for the formation of colored complex. I_x and I_y were the light intensities transmitted by two solutions of concentrations x and y of colored complex when the second component had the respective concentrations b and d, and n was the number of moles of the second component uniting with one mole of the first component of concentration a to give the colored complex.

Equation (2) is valid when I_0 is unity. In American-made optical instruments I_0 is not taken as unity but as 100 and the transmission I/I_0 is read in per cent. The expression for y/x becomes

$$\frac{y}{x} = \frac{\log I_y/I_0}{\log I_x/I_0} \tag{3}$$

and the general equation for K is then

$$K = \frac{b^n d^n (\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y + \log I_0 (b^n - d^n)} \tag{4}$$

and for $I_0 = 100$ we have

$$K = \frac{b^n d^n (\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y + 2(b^n - d^n)} \tag{5}$$

If I_x and I_y refer to fractions of transmitted light, equation (2) is correct. The symbol I, however, ordinarily represents intensity of light.

[1] Work supported by the Office of Naval Research under contract with the Institute of Science and Technology of the University of Arkansas.

[2] S. M. Edmonds and N Birnbaum, This Journal, **63**, 1471 (1941).

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The Preparation and Characterization of Some Deuteroboron Compounds

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In relation to physical-structural studies on borine carbonyl[1] and dimethylaminodiborane,[2] it was necessary to employ the B-deuterated varieties for comparison purposes. Accordingly B_2D_6 was prepared and converted to the desired compounds. Some physical properties of these and incidental by-products are described in this note. It appears that the melting points and vapor tensions of most of the deutero-compounds differ enough from those of the protium compounds for use in assaying the results of tracer studies involving these substances.

Pure B_2H_6.—Diborane was prepared by the use of lithium aluminum hydride.[3] After a preliminary distillation in the high-vacuum apparatus at the lowest feasible temperature, it was purified by forming the unstable $(CH_3)_2OBH_3$ at −78.5°;[4] the impurities were pumped off at −100° and the diborane recovered from the decomposing complex by distillation through a trap at −150°. As a final step, the diborane was left for an hour at −78.5°, to form the complex from any remaining trace of methyl ether, and then distilled from a tube at −160°. This was the procedure which yielded the sample in which the mass-spectrograph showed no impurity.[5] The vapor tension at −111.9° was observed as 225.0 mm. (cor.).

B_2D_6.—Pure diborane was deuterated by successive treatments with samples of deuterium generated from 99.8% pure D_2O, until calculation indicated 98% replacement. Equilibrium at each stage was assured by heating the mixture in a previously baked-out Pyrex bulb for 24 hours at 75°—conditions far more energetic than those suggested by studies of the rate of exchange.[6] The 98% B_2D_6 had a vapor tension of 238.3 mm. (cor.) at −111.9°, in agreement with a private communication from H. I. Schlesinger and B. Rice.

Pentaborane.—Occasional overheating of the exchanging mixtures led to minor yields of deuterated pentaborane; a sample between $B_5H_2D_7$ and B_5HD_8 had a vapor tension of 67.5 mm. at 0°—definitely above the rechecked value of 66 mm. for B_5H_9.[7]

$(CH_3)_2OBD_3$.—It was noticed also that the methyl ether complex formed from 85% deuterated diborane had a dissociation pressure of 30 mm. at −78.5°; by comparison with the 18 mm. value for $(CH_3)_2OBH_3$,[4] this result would indicate 32 mm. for pure $(CH_3)_2OBD_3$ in equilibrium with B_2D_6 and $(CH_3)_2O$ at −78.5°. The 80% increase of dissociation pressure upon deuteration suggested the possibility of separating partially deuterated diborane into light and heavy fractions, since the reaction $B_2H_6 + 2(CH_3)_2O \rightarrow 2(CH_3)_2OBH_3$ would be most favored for the least deuterated material. In an actual test, a 75% deuterated sample of diborane was separated into 70 and 80% fractions by overnight treatment with an equal gas-volume of methyl ether at −78.5°, with recovery of the lighter half of the original sample by decomposition of the complex. However, such a process would become very tedious for purification of B_2D_6, since the absolute separation decreases sharply as the D-content increases.

$(CH_3)_2ND$.—Before $(CH_3)_2NB_2D_5$ could be prepared by the usual aminolysis,[8] it was necessary to prepare $(CH_3)_2ND$, since the use of $(CH_3)_2NH$ would have led to HD, and an exchange with the B–D bonds in the product would mean serious contamination. That such an exchange actually does occur under the preparative conditions was shown by heating a 22-cc. sample of $(CH_3)_2NB_2H_5$ with 115 cc. of D_2 (gases at S.C.) for 74 hours at 100°; then after repurification, the dimethylaminodiborane showed an increase of vapor tension from the original 101.2 to 103.8 mm. at 0°. Subsequent studies of nearly pure $(CH_3)_2NB_2D_5$ showed that this result corresponded to 65% deuteration (calcd., 67%). Accordingly, $(CH_3)_2ND$ was prepared by the room temperature reaction of $[(CH_3)_2N]_2BH$ with 99.8% D_2O. An exchange contamination of the product by the action of HD

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[1] W. Gordy, H. Ring and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

[2] D. E. Mann and B. L. Crawford, Jr., unpublished.

[3] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, This Journal, **69**, 1201 (1947).

[4] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 296 (1938).

[5] V. H. Dibeler and F. L. Mohler, *ibid.*, **70**, 988 (1948).

[6] A. N. Webb, J. T. Neu and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1949).

[7] A. Stock and W. Siecke, *Ber.*, **57B**, 570 (1924).

[8] A. B. Burg and C. L. Randolph, Jr., This Journal, **71**, 3452 (1949).

apparently did not occur, since the use of heat (100°) to complete the reaction gave the same purity as the room temperature reaction, and the final product had a vapor tension of 546.6 mm. (cor.) at 0°—nearly 1 mm. lower than the literature value,[9] and suggesting slightly higher purity.

$(CH_3)_2NBD_2$.—The compound $(CH_3)_2NBD_2$ was prepared by heating 112.2 cc. of B_2D_6 and 203.7 cc. of $(CH_3)_2ND$ (gases at S.C.) in a sealed 300-cc. bulb for 6 hours at 137°. After separation of the $(CH_3)_2NBD_2$ (90% yield) from the by-product $(CH_3)_2NB_2D_5$, the m.p. of the former was observed as 74.3–74.5°—within the half-degree experimental error of the m.p. of pure $(CH_3)_2NBH_2$.[8] The vapor tension at 0° may have been 2% higher than that of $(CH_3)_2NBH_2$.

$(CH_3)_2NB_2D_5$.—More B_2D_6 now was added to the $(CH_3)_2NBD_2$ at 106° (12 hours), quantitatively forming $(CH_3)_2NB_2D_5$. This showed a vapor tension of 105.2 mm. at 0°, or 4.0 mm. higher than $(CH_3)_2NB_2H_5$. Its m.p. was −57.0° —a drop of 2.4° below $(CH_3)_2NB_2H_5$.[8]

BD_3CO.—The compound BD_3CO was prepared in 85% yield by treating B_2D_6 (one atm.) in a bomb tube with CO (ten atm.) during one week at room temperature. Since it is less volatile than BH_3CO, while B_2D_6 is more volatile than B_2H_6, the purification, by fractional condensation at −150°, proved to be easier than in the case of BH_3CO. The m.p. of BD_3CO was observed as −134.4° (2.6° above that of BH_3CO).[10] The vapor tensions of BD_3CO at three widely different temperatures, determining the equation $\log_{10} p_{\text{mm.}} = 7.810 - 1040/T$ are given in Table I. This equation implies the same heat of vaporization as for BH_3CO; only the entropy factor is slightly smaller. Even the downward-concavity of the curve of log p *vs.* $1/T$ is nearly the same for both substances.

TABLE I

VAPOR TENSIONS OF DEUTEROBORINE CARBONYL

t (°C.)	−111.85	−95.5	−95.4	−78.5
p_{mm} (obsd.)	23.0	90.6	91.4	294
p_{mm} (calcd.)	23.0	92.0	93.0	294
v.t. of BH_3CO [10]	25.4	99.2	100.2	322

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[9] E. R. Roberts, H. J. Emeléus and H. V. A. Briscoe, *J. Chem. Soc.*, 41 (1939).

[10] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 782 (1937).

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Oxidation Potential of the Pu(III)–Pu(IV) Couple in Perchloric and Hydrochloric Acid

BY ROBERT E. CONNICK AND W. H. MCVEY

It was pointed out by Rabideau and Lemons[1] that the value given by us[2] for the Pu(III)–Pu(IV) formal potential in 1 *M* hydrochloric acid is in error. The mistake, which arose from a typographical error in an earlier paper,[3] makes necessary a change of the hydrochloric acid potential scheme and the discussion of chloride complexing.

The formal potential scheme for 1 *M* hydrochloric acid at 25° becomes

$$\underbrace{\mathrm{Pu(III)}\ \overset{-0.969}{\text{————}}\ \mathrm{Pu(IV)}\ \overset{-1.052}{\text{————}}\ \mathrm{Pu(VI)}}_{-1.024}$$

Our value for the Pu(III)–Pu(IV) couple differs 2 millivolts from that of Rabideau and Lemons because of a different weighting of the original experimental data of Hindman and because we used an activity coefficient of hydrochloric acid based on moles per liter of solution rather than moles per 1000 g. of water.

The per cent. Pu(IV) complexed by chloride ion at 25° in 1 *M* hydrochloric acid becomes 40%.

The anomaly of a more negative potential for the Pu(III)–Pu(VI) couple in hydrochloric acid than in perchloric acid is now intensified. We believe the discrepancy arises primarily from an error in the Pu(III)–Pu(IV)–Pu(VI) equilibrium constant caused by reduction of Pu(IV) to Pu(III) by the products of the α-particles of the plutonium. This effect is more important in one molar perchloric acid than in hydrochloric acid and accounts for the major part of the discrepancy. A fuller account will be published.

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[1] S. W. Rabideau and J. F. Lemons, THIS JOURNAL, **73**, 2895 (1951).

[2] R. E. Connick and W. H. McVey, *ibid.*, **73**, 1798 (1951).

[3] R. E. Connick, Manhattan Project Report CC-3869 (May 5, 1948).

Methylation of Partially Methylated Sugar Anilides[1]

BY I. EHRENTHAL, M. C. RAFIQUE AND F. SMITH

In an attempt to ascertain the ring structure of sugar anilides,[2] Irvine and Gilmour were able to show that when D-glucose anilide was treated with silver oxide and methyl iodide some 2,3,4,6-tetramethyl-D-glucose anilide could be isolated in spite of the fact that oxidation occurred and repeated treatment was necessary.[3] Methylation can also be carried out with methyl sulfate.[4]

For some time we have been making use of an extension of this reaction to partially methylated sugar anilides.[5,6] Whether the latter are crystalline or not most of them undergo complete methylation with silver oxide and methyl iodide to give good yields of the corresponding crystalline fully methylated sugar anilides which have proved to be valuable in the characterization of sugars. The reaction proceeds best with those partially methylated anilides which are soluble in methyl iodide but it can also be applied to those which require methanol or acetone to dissolve them.

Inasmuch as the crystalline anilides of the fully methylated sugars have pyranose structures it would appear, if it can be assumed that no change in ring form occurs during methylation, that most if not all the anilides of partially methylated sugars also have a pyranose structure.

In most instances in the past, the characterization of the parent sugar of an unknown partially methylated derivative has involved its complete methylation to give the fully methylated methyl glycoside which was hydrolyzed to give the fully methylated

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[1] Paper No. 2694, Scientific Journal Series, Minnesota Agricultural Experiment Station.

[2] B. Sorokin, *Ber.*, **19**, 513 (1886); *J. prakt. Chem.*, [2] **37**, 291 (1888).

[3] J. C. Irvine and R. Gilmour, *J. Chem. Soc.*, **93**, 1429 (1908).

[4] G. P. Ellis and J. Honeyman, *Nature*, **167**, 239 (1951).

[5] F. Smith, THIS JOURNAL, **70**, 3249 (1948).

[6] M. C. Rafique and F. Smith, *ibid.*, **72**, 4634 (1950).