apparently did not occur, since the use of heat  $(100^\circ)$  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  $0^\circ$ —nearly 1 mm. lower than the literature value,<sup>9</sup> and suggesting slightly higher purity. (CH<sub>3</sub>)<sub>2</sub>NBD<sub>2</sub>.—The compound (CH<sub>3</sub>)<sub>2</sub>NBD<sub>2</sub> was prepared by heating 112.2 cc. of B<sub>2</sub>D<sub>6</sub> and 203.7 cc. of (CH<sub>3</sub>)<sub>2</sub>-ND (crease at SC) in a sealed 200.cc with for 6 hours at

 $(CH_3)_2NBD_2$ .—The compound  $(CH_3)_2NBD_2$  was prepared by heating 112.2 cc. of  $B_2D_6$  and 203.7 cc. of  $(CH_3)_2$ -ND (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  $(CH_3)_2NBH_2$ .<sup>8</sup> The vapor tension at 0° may have been 2% higher than that of  $(CH_3)_2NBH_2$ .

observed as 74.3-74.5 — within the half-degree experimental error of the m.p. of pure  $(CH_3)_2NBH_2$ .<sup>8</sup> 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  $(CH_3)_2$ . NBD<sub>2</sub> at 106° (12 hours), quantitatively forming  $(CH_3)_2$ -NB<sub>2</sub>D<sub>5</sub>. 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  $-57.0^{\circ}$ —a drop of 2.4° below  $(CH_3)_2NB_2H_5$ .<sup>8</sup> BD<sub>3</sub>CO.—The compound BD<sub>2</sub>CO was prepared in 85% wield by treating B-D<sub>2</sub> (one atm ) in a bomb tube with CO

**BD**<sub>3</sub>**CO**.—The compound BD<sub>3</sub>**CO** was prepared in 85% yield by treating B<sub>2</sub>D<sub>6</sub> (one atm.) in a bomb tube with CO (ten atm.) during one week at room temperature. Since it is less volatile than BH<sub>3</sub>CO, while B<sub>2</sub>D<sub>6</sub> is more volatile than B<sub>2</sub>H<sub>6</sub>, the purification, by fractional condensation at  $-150^{\circ}$ , proved to be easier than in the case of BH<sub>3</sub>CO. The m.p. of BD<sub>3</sub>CO was observed as  $-134.4^{\circ}$  (2.6° above that of BH<sub>3</sub>CO).<sup>10</sup> The vapor tensions of BD<sub>3</sub>CO at three widely different temperatures, determining the equation log<sub>10</sub>  $p_{mm}$ . = 7.810 - 1040/T are given in Table I. This equation implies the same heat of vaporization as for BH<sub>3</sub>-CO; 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

<i>t</i> (°C.)	-111.85	-95.5	-95.4	-78.5
$p_{mm}$ (obsd.)	<b>23</b> .0	90.6	91.4	294
$p_{mm}$ (calcd.)	23.0	92.0	93.0	294
v.t. of BH <sub>3</sub> CO 10	25.4	99.2	100.2	322

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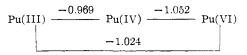
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## Oxidation Potential of the Pu(III)-Pu(IV) Couple in Perchloric and Hydrochloric Acid

## BY ROBERT E. CONNICK AND W. H. MCVEY

It was pointed out by Rabideau and Lemons<sup>1</sup> 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,<sup>3</sup> 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  $25^{\circ}$  becomes



<sup>(1)</sup> S. W. Rabideau and J. F. Lemons, THIS JOURNAL, 73, 2895 (1951).

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

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  $\alpha$ -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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## Methylation of Partially Methylated Sugar Anilides<sup>1</sup>

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

In an attempt to ascertain the ring structure of sugar anilides,<sup>2</sup> 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.<sup>3</sup> Methylation can also be carried out with methyl sulfate.<sup>4</sup>

For some time we have been making use of an extension of this reaction to partially methylated sugar anilides.<sup>5,6</sup> 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

(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).

<sup>(2)</sup> R. E. Connick and W. H. McVey, *ibid.*, 73, 1798 (1951).