

can be only partially oxidized by a ferro-ferri-cyanide oxidation-reduction buffer (20:1) under conditions which permit complete oxidation of II. (d) The cathodic mobility of I on ionophoresis in 1% ammonium acetate on Whatman no. 5 paper is less than that of II by at least one order of magnitude.

Preparations of I, as obtained by the Keilin-Hartree procedure, usually exhibit a purity of 10-50%, based on spectral absorption properties and the assumption that the extinction coefficients at the characteristic absorption maxima are closely similar to those for II. Electrophoretic treatment of such preparations results in a 2- or 3-fold purification because of removal of colorless impurities which migrate rapidly toward the cathode.

The conclusion that I is not identical with II is further strengthened by the observation that I can be oxidized via mammalian cytochrome oxidase, if some II is added to the reaction mixture (see Fig. 1). Complete oxidation in this manner cannot be attained, indicating in agreement with (c) above, that the oxidative-reduction potential of I is slightly positive with respect to II.

It is tempting, but premature, to discuss the many intriguing possibilities raised by the presence of this new cytochrome in photosynthetic organisms. We may note, however, that the existence of the bacterial cytochrome may provide the basis for a mechanism of photochemical H-transport and an explanation for the absence of a light-stimulated respiration in the photoheterotrophes. It is suggested that I be called tentatively "cytochrome-c2".<sup>3</sup> Further researches on the properties of this and other haem-proteins in the photosynthetic bacteria are proceeding.

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(3) R. Hill and D. Keilin, private communication.

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#### BEHAVIOR OF AN ION-EXCHANGE RESIN IN LIQUID AMMONIA

Sir:

In the course of a study of ion species present in liquid ammonia solution, use has been made of the cation exchange resin Dowex-50.<sup>1</sup> The ammonium form of the resin, dried 16 hours *in vacuo*, was washed copiously at  $-33^{\circ}$  by repeatedly condensing fresh anhydrous ammonia upon it and then filtering. The resin was exposed, in a column operation, to a solution of liquid ammonia which contained the products of the reaction of potassium

(1) These studies were inspired by a paper which described the use of a cation exchange column in the study of  $\text{KBF}_3\text{OH}$ : see C. A. Wamser, *THIS JOURNAL*, **73**, 419 (1951).

with monoammino boron trifluoride<sup>2,3</sup> (0.1901 g. K, 0.4380 g.  $\text{BF}_3\cdot\text{NH}_3$ ).

The total product from the 0.6281 g. of reactants dissolved in about 35 ml. of ammonia, was passed through a resin column, one  $\text{cm.}^2 \times 12$  cm. at a rate that varied between 1 and 2 ml. per minute. The resin, which was largely in the ammonium form, quantitatively removed potassium from the solution. Boron and fluorine passed through the resin bed. The eluate solution was evaporated to dryness and the solid residue, which weighed 0.4457 g. after evacuation, was shown to be mainly  $\text{BF}_3\cdot\text{NH}_3$  by X-ray diffraction analysis.<sup>4</sup>

After the resin column had been washed until the washings gave negative tests for boron, a solution of ammonium chloride was passed through the column. The 11.7 g. of resin had a calculated capacity of 58.5 meq. cation, 10.9 meq. of potassium being on the resin after two exchange experiments. The passage of a total of 134 meq. ammonium ion (in approx. 1.5 M  $\text{NH}_4\text{Cl}$  solution) through the column resulted in the elution of only 0.4 meq. potassium.

The behavior of Dowex-50 in liquid ammonia parallels its behavior in water. A solution of ammonium chloride in ammonia behaves like a solution of hydrogen chloride in water: neither are efficient in stripping the resin of potassium ions. Potassium ion efficiently displaces ammonium ion from the resin in ammonia just as it displaces hydronium ion from the resin in water solution.

It appears that ion-exchange techniques of separations, purifications, and syntheses can be used successfully in the liquid ammonia medium.

(2) In a forthcoming publication it will be shown that  $\text{BF}_3\cdot\text{NH}_3$  reacts with *only one* equivalent of potassium in dilute ammonia solutions. When the resulting solution is evaporated to dryness and analyzed by X-ray diffraction the pattern of KF is found. Quantitative recovery of the total solid products and analysis of the gaseous and solid products support the following interpretation:



This equation accounts for all our observations, but it is emphasized that we have not as yet isolated the boron compound.

(3) For a description of the reaction of sodium with  $\text{BF}_3\cdot\text{NH}_3$  in liquid in ammonia see C. A. Kraus and E. H. Brown, *ibid.*, **51**, 2690 (1929).

(4) The X-ray powder diffraction of  $\text{BF}_3\cdot\text{NH}_3$  as obtained in this laboratory does not check with that reported by A. W. Laubengayer and G. F. Condikey, *ibid.*, **70**, 2274 (1948). As prepared here in two ways, or as recrystallized from either water or liquid ammonia, the compound yields the following lines:

4.87 (m) 4.01 (s) 3.65 (s) 3.37 (s) 2.87 (m) 2.72 (s)  
2.45 (m) 2.34 (m) 2.24 (s) 1.97 (w) 1.81 (m) 1.65 (w)

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#### THE STRUCTURE OF PITHECOLOBINE

Sir:

Some time ago we described an alkaloid from the bark of *Pithecolobium saman* (Benth.)<sup>1</sup>  $\text{C}_{22}\text{H}_{48}\text{N}_4\text{O}_2$  (one amide group, one hydroxy group, one ring, no double bond) which on reduction with  $\text{LiAlH}_4$  gave desoxypithecolobine  $\text{C}_{22}\text{H}_{48}\text{N}_4$  (one ring, no double bond). Analytical difficulties with even highly

(1) K. Wiesner, D. M. MacDonald, Z. Valenta and R. Armstrong, *Can. J. Chem.*, **30**, 761-772 (1952).