

As yet it is not known whether the formation of mixed organolithium compounds will occur generally. Preliminary results indicate that *t*-butyllithium enhances the solubility of phenyllithium in benzene, but only to a limited extent.

**Acknowledgments.**—We are indebted to Dr. E. B. Baker of the Dow Chemical Co. and Dr. Ronald Baney of the Dow-Corning Corporation for the measurements of lithium-7 n.m.r. spectra, and to the Atomic Energy Commission for financial support.

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RECEIVED JANUARY 7, 1963

**ADSORPTION ON INORGANIC MATERIALS. V.  
REACTION OF CADMIUM SULFIDE WITH COPPER(II),  
MERCURY(II) AND SILVER(I)<sup>1,2</sup>**

Sir:

In continuation of our studies of the adsorption and ion exchange properties of insoluble inorganic materials, we have examined a number of sulfides for possible chromatographic use. The present note deals with the properties of cadmium sulfide which was found to be an excellent "adsorbent" for heavy metal ions such as Cu(II), Hg(II) and Ag(I) which form highly insoluble sulfides. While the reaction of CdS with ions of this type has long been known,<sup>3</sup> apparently it has not been recognized before that the reaction is fast enough for chromatographic use in aqueous media.

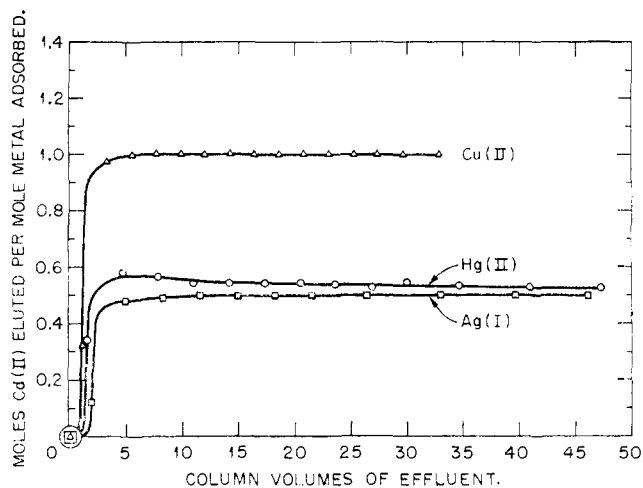


Fig. 1.—Reaction of various heavy metal ions with cadmium sulfide columns (25°; columns: ca. 0.2 cm.<sup>2</sup> × 2 cm., flow rate ca. 2 cm./min.).

Cadmium sulfide was prepared by addition, with continuous stirring, of excess ammonium sulfide to a 0.2 M cadmium nitrate solution. The resulting precipitate was collected by filtration and washed with water, 0.2 M HNO<sub>3</sub>, and again with water. The material was dried at 25°, ground, and sieved (mesh size, 80–170). This sieved material gave columns which have good flow characteristics. The columns had a cross-sectional area of ca. 0.2 cm.<sup>2</sup> and were ca. 2 cm. high. X-Ray crystallographic examination of the material<sup>4</sup> revealed only lines of the cubic CdS; the crystallite size was about 90 Å.

(1) This document is based on work performed for the U. S. Atomic Energy Commission and for the Office of Saline Water, U. S. Department of the Interior, at the Oak Ridge National Laboratory, Oak Ridge, Tennessee, operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

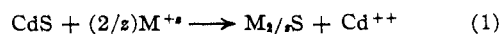
(2) Previous paper: H. O. Phillips and K. A. Kraus, *J. Am. Chem. Soc.*, **84**, 2267 (1962).

(3) E. Schürmann, *Lieb. Ann.*, **249**, 326 (1888).

(4) We are indebted to Robert L. Sherman of ORNL Analytical Chemistry Division for the crystallographic examinations.

When dilute (*e.g.*, tracer) or concentrated (*e.g.*, 1 M) solutions of silver, copper or mercury nitrates, with or without supporting electrolyte (NaNO<sub>3</sub>, HNO<sub>3</sub>), were passed through columns of cadmium sulfide, quantitative removal of the ions from the solution was obtained as determined by radiometric analysis of the effluent (Ag<sup>110</sup>, Hg<sup>203</sup>, Cu<sup>64</sup>). The adsorption reaction is insensitive to the anions present in the solution; in the case of Ag(I) (0.05 M), excellent adsorption was found even from 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> in which Ag(I) is strongly complexed.

Adsorption of these ions by cadmium sulfide might be expected to result principally from displacement reactions of the type



To establish the stoichiometry of the reaction, a series of column experiments was carried out with 0.050 M AgNO<sub>3</sub>–1.0 M NaNO<sub>3</sub>, 0.052 M Cu(NO<sub>3</sub>)<sub>2</sub>–0.004 M HNO<sub>3</sub> and 0.050 M Hg(NO<sub>3</sub>)<sub>2</sub>. The effluent was analyzed for Cd(II) by EDTA titrations<sup>5</sup> while absence of the other heavy metal ions was confirmed radiometrically. Except for a slight delay in Cd(II) breakthrough, the reaction with Ag(I) and Cu(II) follows equation 1 quantitatively as shown in Fig. 1. With Hg(II), the effluent Cd(II) concentration was substantially less than expected from equation 1.

Qualitatively, excess adsorption of Hg(II) over that expected from equation 1 would be expected if there is at least partial formation of double salts of the type (HgS)<sub>n</sub>HgX<sub>2</sub>. White double salts with composition (HgS)<sub>2</sub>HgX<sub>2</sub> are well known.<sup>6</sup> Treatment of CdS and HgS columns with excess of Hg(II) solutions yielded white or gray solids, suggesting formation of such double salts. However, the amount of Hg(II) adsorbed by CdS in the experiment described in Fig. 1 is in excess of that expected for formation of (HgS)<sub>2</sub>Hg(NO<sub>3</sub>)<sub>2</sub>; perhaps basic double salts containing a still larger Hg/S ratio are formed.

The reaction between CdS and the heavy metal ions often goes essentially to completion under the usual conditions of column operation. Thus silver uptake as high as 13.2 moles per kilogram of CdS was achieved with a 0.21 cm.<sup>2</sup> × 1.45 cm. CdS column with 0.05 M AgNO<sub>3</sub>–1 M NaNO<sub>3</sub>–0.001 M HNO<sub>3</sub> at a flow rate of 5 cm./min. This uptake is equivalent to a 94% conversion to Ag<sub>2</sub>S. Conversion to CuS is somewhat slower; at the same flow rate using a similar column and 0.052 M Cu(NO<sub>3</sub>)<sub>2</sub>–0.004 M HNO<sub>3</sub>, 4.7 moles of Cu(II) was adsorbed at 50% breakthrough, which is equivalent to 70% of theoretical (6.92 moles per kg.).

The extreme rapidity with which the adsorption-displacement reactions proceed is probably the most striking feature in the chromatographic application of CdS. Thus, using 0.05 M Ag(I) and Cu(II) solutions, quantitative adsorption was found with 2 to 3 cm. columns at flow rates up to 50 cm./min. During the adsorption, a color change occurs from orange to black; the boundary remains remarkably sharp at flow rates as high as 25 cm./min. With Hg(II) the reactions are more complicated and not quite as fast. A red HgS, which often forms first, slowly converts to the black sulfide and it in turn converts still more slowly (at room temperature) to the white double salts.

Cadmium sulfide, in view of its high capacity, applicability to dilute and concentrated solutions, and very favorable exchange kinetics thus seems to be a very

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(6) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 4, Longmans, Green and Co., New York, N. Y., New Impression, 1952, p. 961.

useful material for the recovery of a large number of heavy metals which form insoluble sulfides.

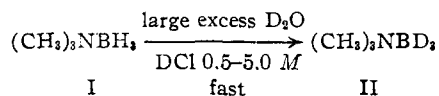
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RECEIVED JANUARY 16, 1963

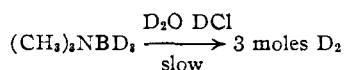
### A RAPID AND QUANTITATIVE EXCHANGE OF THE BORON HYDROGENS IN TRIMETHYLAMINE BORANE WITH D<sub>2</sub>O<sup>1</sup>

Sir:

Close examination of the slow acidic hydrolysis of trimethylamine borane<sup>2-4</sup> and the most noteworthy absence of a boron-hydrogen kinetic isotope effect<sup>3</sup> has demonstrated now that the boron hydride hydrogens are *exchanging* with the protons of the solvent.



The homogeneous reaction of I in dilute deuteriochloric acid first produces II which can be extracted with ether or allowed to hydrolyze slowly to produce pure deuterium gas.



In keeping with these data the hydrolysis of trimethylamine borane-*d*<sub>3</sub> in hydrochloric acid produces only hydrogen gas.

No other simple derivatives of diborane have been reported to exchange with heavy water.<sup>5</sup> As I has been used to reduce carbonyl compounds and hydroborate olefins,<sup>6-8</sup> the exchange reaction now allows convenient reductive deuterations using heavy water as the source of deuterium. Norcamphor, benzophenone, cyclohexanone and acetone have been reduced to the  $\alpha$ -deuterio alcohols using II and boron trifluoride etherate.<sup>7</sup> Deuterioborations have been performed in refluxing toluene.<sup>8</sup> Trimethylamine borane-*d*<sub>3</sub> also has been converted into sodium borodeuteride using sodium methoxide in diglyme.

Large amounts of trimethylamine-*d*<sub>3</sub> are obtained readily using this procedure: sulfuryl chloride (0.50 ml.) is vigorously stirred for twenty minutes with 20 ml. of heavy water. Trimethylamine borane (Callery Chemical Co., 1.000 g., 13.9 mmole) dissolved in fifty ml. of ether is vigorously stirred with the acidic heavy water at 25°. The exchange reaction is followed by infrared analysis. The extent of hydrolysis is determined manometrically. After six hours the deuterium content of the amine borane is 98% while less than 6% has hydrolyzed. The ether layer is dried over potassium carbonate.<sup>9</sup> Evaporation *in vacuo* leaves a white residue which is sublimed. The product weighs 0.997 g. (m.p. 94°, undepressed with I, 98.1% deuterium by mass spectrum).

(1) Boron Hydrides. VI. Paper V, R. E. Davis and J. A. Gottbrath, *J. Am. Chem. Soc.*, **84**, 895 (1962).

(2) G. E. Ryschkewitsch, *ibid.*, **82**, 3290 (1960).

(3) R. E. Davis, C. L. Kibby and C. G. Swain, *ibid.*, **82**, 5950 (1960).

(4) R. E. Davis, *ibid.*, **84**, 892 (1962).

(5) Decaborane will produce B<sub>10</sub>H<sub>10</sub>D<sub>4</sub>: G. A. Guter and G. W. Schaeffer, *ibid.*, **78**, 3546 (1956); R. Atterberry, *J. Phys. Chem.*, **62**, 1457 (1958); R. J. F. Palchak, J. H. Norman and R. E. Williams, *J. Am. Chem. Soc.*, **83**, 3380 (1961). The B<sub>11</sub>H<sub>12</sub><sup>-2</sup> ion will completely exchange with heavy water (E. L. Muettterties, R. D. Menifield, H. C. Miller, W. H. Knoth, Jr., and J. R. Downing, *ibid.*, **84**, 2506 (1962)). Neither has found application as a useful reducing agent in organic chemistry.

(6) E. C. Ashby, *ibid.*, **81**, 4791 (1959).

(7) W. M. Jones, *ibid.*, **82**, 2528 (1960).

(8) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover and G. Zweifel, *ibid.*, **82**, 4233 (1960).

(9) This solution can be used directly since the amount of II can be calculated from the amount of gas produced.

These new procedures should greatly facilitate the synthesis of compounds labeled with deuterium or tritium with known stereochemistry to aid in the elucidation of reaction mechanisms.

**Acknowledgment.**—The present study was supported by a Frederick Gardner Cottrell grant from the Research Corporation and a grant from the Sloan Foundation. Discussion with Prof. R. W. Parry is appreciated.

(10) Alfred P. Sloan Fellow, 1962-1964.

(11) This study was begun by Miss A. E. Brown as an undergraduate research problem.

(12) National Science Foundation Predoctoral Cooperative Fellow, 1961-1963.

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RECEIVED JANUARY 14, 1963

### ISOLATION OF ANTIBODY BY MEANS OF AN IMMUNOLOGICAL SPECIFIC ADSORBENT

Sir:

As the immunochemist strives for a better understanding of the physicochemical factors involved in antigen-antibody interactions, the need for purified reactants becomes apparent. In his search he has devised a number of non-specific and specific techniques to obtain purified preparations of antibody. The non-specific methods are based on the fractionation of serum to provide a purified preparation of  $\gamma$ -globulin, and include such methods as ammonium sulfate<sup>1,2</sup> or alcohol fractionation,<sup>3</sup> electrophoresis<sup>4</sup> and column chromatography on DEAE-cellulose.<sup>5</sup> Although these techniques provide fairly pure  $\gamma$ -globulin preparations the specific immune  $\gamma$ -globulin desired may be only a small percentage of the total protein in the purified preparation. Hence, one obtains a good yield but low purity with respect to antibody.

The specific methods of antibody purification involve the removal of antibody by precipitation with the specific soluble antigen or reaction of antiserum with antigen in some insoluble state, and subsequent dissociation of the antibody from the precipitate by one of several methods.<sup>6-9</sup> Many of these specific methods depend upon some special property (*i.e.*, insolubility of the antigen in high salt concentration, mercurial salts, etc.) of the particular antigen-antibody system and therefore limit their applicability. The more general method of alkaline dissociation of antigen-antibody precipitates often leads to denaturation of the antibody, and particularly upon prolonged contact with the antibody. The method of acid dissociation<sup>10</sup> of antigen-antibody precipitates at pH 3.0 has been used by many investigators, and seems to be the most applicable. However, the soluble protein antigens must be rendered insoluble by some other procedure such as

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(8) L. A. Steinberger and D. Pressman, *J. Immunol.*, **65**, 65 (1950).

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(10) D. H. Campbell and F. Lanni in D. M. Greenberg, "Amino Acids and Proteins," 1st ed., Charles C. Thomas, Springfield, Ill., Chapter XI, 1951.