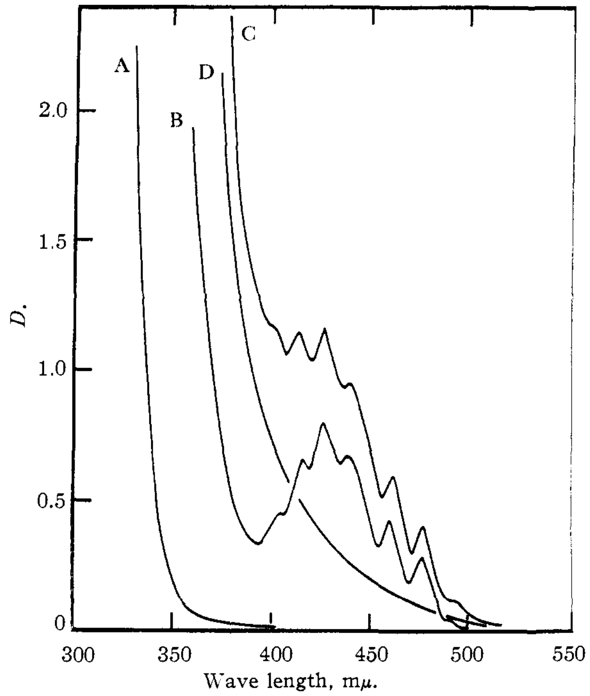

Fig. 2.—Interaction absorption of U(VI) and Sn(II): A, 1 *M* Sn(II); B, 0.1 *M* U(VI); C, 0.1 *M* U(VI); 1 *M* Sn(II); D = C–A–B. All 6 *M* HCl, 5 mm. cells.

maximum indicates that the complex is very largely dissociated.

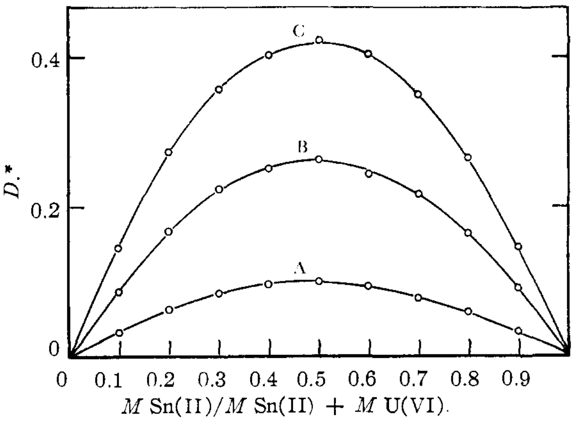

Fig. 3.—Method of continuous variations: total Sn(II) + U(VI) = 1 *M*. All solutions 7 *M* HCl, 1 mm. path length cells. $D^* = D_{\text{total}} - D_{\text{U(VI)}} - D_{\text{Sn(II)}}$. A, 455 mμ; B, 420 mμ; C, 400 mμ.

An analysis of these data by the method of Davidson is shown in Fig. 4 where the interaction absorption is plotted *versus* the product of the total Sn(II) and total U(VI) concentrations. The fact that a straight line is obtained indicates that the complex not only has a 1:1 composition but that it actually contains one U(VI) and one Sn(II) and that its concentration is inappreciable compared to that of the reactants. (Otherwise it would be necessary to correct the tin and uranium concentrations for the amount reacted.) Unfortunately, it is not possible to determine the instability constant of the complex from either analysis, but only the product of this by the extinction coefficient for any given wave length.

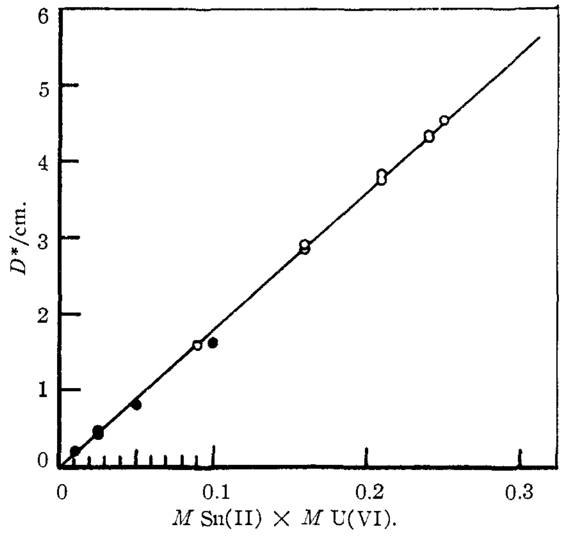

Fig. 4.—Variation of D^* with Sn(II), U(VI) product: ●, 5 mm. cells; ○, 1 mm. cells. All 7 *M* HCl, 400 mμ wave length.

The composition of the interaction complex and the first-order dependence of the reduction reaction on U(VI) and Sn(II) suggests, but does not prove, that the observed complex may be an intermediate in the reduction reaction and that its decomposition may constitute the rate controlling step.

Other Uranium–Tin Complexes.—Addition of either Sn(II) or Sn(IV) to a U(IV) solution (prepared by electrolytic reduction at a mercury cathode) resulted in no change in the U(IV) absorption in the visible region. However a weak interaction between U(IV) and Sn(II) was found in the ultraviolet around 320 to 340 mμ near the Sn(II) cutoff. Here, too, a 1:1 complex was indicated. The intense ultraviolet absorption of traces of U(III), formed by over reduction in the electrolytic cell, or of traces of U(VI), formed by air oxidation of U(IV), prevented the detection of interaction between U(IV) and Sn(IV).

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GENERAL ELECTRIC COMPANY
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A Convenient Preparation of Pyridine–Borane

BY MODDIE D. TAYLOR, LOUIS R. GRANT AND CLIFTON A. SANDS

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Pyridine–borane, $C_5H_5NBH_3$, is a pale yellow liquid which freezes to a white solid of melting point 10–11°. It is stable in dry air, nearly insoluble in water, only slightly hydrolyzed by it, and very soluble in alcohol and ether. It is an excellent reducing agent: reducing iron to the ferrous state in slightly acid solution; silver nitrate to silver; and iodine to iodide, giving rise to lower iodides of boron at the same time. Its high solubility in ether coupled with its great stability and low reactivity in neutral and alkaline solutions should render it a very convenient reducing agent for organic compounds.[1]

Schlesinger and co-workers[2] have described the preparation of a 1.0-ml. sample of pyridine–borane from the reaction of pyridine and diborane at room temperature. They report its melting point as 10–11° and list some vapor pressures. A very convenient method for the preparation of this compound has been developed in this Laboratory. It is similar to one developed by Schaeffer[3] for the preparation of trimethylamine–borane except that a safer solvent than ether, pyridine, is used; a cheaper and more readily available reagent than $LiBH_4$, $NaBH_4$, is used; and a simpler method for separating the reaction products is available.

The reaction for the preparation of pyridine–borane follows the equation

$$C_5H_5N{\cdot}HCl + NaBH_4 \longrightarrow C_5H_5NBH_3 + NaCl + H_2$$

Sodium chloride precipitates quantitatively from the pyridine solution of pyridine–borane and the two can be separated readily by filtration. The excess pyridine is distilled away under vacuum at 50°. Unreacted $C_5H_5N{\cdot}HCl$ is precipitated by the addition of an equal volume of ether. The ether pumped off and the treatment repeated. Two or three such treatments yield pure pyridine–borane. Alternatively, the crude pyridine–borane can be purified by shaking with water, in which it is insoluble and with which it does not react readily, to dissolve any contaminating NaCl or $C_5H_5N{\cdot}HCl$. Several preparations of pyridine–borane have been performed. They all yield 80–90% of 95–100% pure compound.

In a typical preparation 65.9 g. of $C_5H_5N{\cdot}HCl$ (0.57 mole)[4] was suspended in 150 ml. of pyridine and treated with 22.14 g. (0.585 mole) of $NaBH_4$ in 575 ml. of pyridine by the usual Grignard technique. The reaction was completed smoothly according to the general procedure outlined above. Forty-nine grams of pyridine–borane was obtained for a yield of 93%. The yield was quantitative based on the NaCl produced (33.2 g.). The crude product was treated once with ether and then extracted with water. A yield of 87% of 99.8% pure $C_5H_5NBH_3$ was obtained.

The identity of pyridine–borane was established by the following analyses: (a) hydrogen evolved during acid hydrolysis amounted to 3.20% (theor. = 3.25); (b) reducing power by the iodate procedure[5] yielded 3.18 and 3.17% H_2; (c) boron by base titration in the presence of mannitol after base hydrolysis to remove pyridine yielded 11.51 and 11.55% (theor. = 11.64); and (d) pyridine by the $CuSO_4$–KCNS technique[6] yielded 84.19 and 84.70% (theor. = 85.11%). In agreement with the findings of Schlesinger and co-workers the compound melted at 10–11°, and exhibited a vapor pressure of less than 0.1 mm. at room temperature. It is quite soluble in ether but insoluble in water. It has an index of refraction of 1.5280 at 25°. It reacts rapidly with acids with the evolution of hydrogen.

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(1) The action of pyridine–borane on certain organic compounds is now under investigation in this Laboratory.

(2) H. C. Brown, H. I. Schlesinger and S. Z. Cardon, THIS JOURNAL, **64**, 328 (1942).

(3) G. W. Schaeffer and E. R. Anderson, *ibid.*, **71**, 2143 (1949).

(4) Pure anhydrous $C_5H_5N{\cdot}HCl$ is readily prepared by treating a solution of pyridine in ether with pure dry HCl, filtering off the excess ether and pumping dry *in vacuo*.

(5) E. Jensen, D. Lyttle and W. Struck, *Anal. Chem.*, **24**, 1843 (1952).

(6) *C. A.*, **19**, 2181 (1924).

New Preparations of Anhydrous Iodides of Groups I and II Metals

BY MODDIE D. TAYLOR AND LOUIS R. GRANT

RECEIVED OCTOBER 1, 1954

Because of the current interest in reactions in non-aqueous solvents anhydrous iodides have assumed importance since their solubility is generally appreciable in such solvents. These compounds are usually not conveniently prepared from their hydrated forms because they tend to pass over to basic iodides during the process of dehydration. Other methods of preparation include the direct reaction of the metal and iodine and the action of ammonium iodide on the metal oxide at elevated temperature. The former reaction is inconvenient because the metal is often not available and the latter, besides being inconvenient because the reaction is between solids at elevated temperature, seldom goes quantitatively to completion and nearly always is contaminated with residual ammonium iodide. Two methods for preparing anhydrous iodides have been developed in this Laboratory. They both are rapid, quantitatively complete and yield a pure iodide. The methods have been applied specifically to lithium and barium iodides but are almost certainly suitable for other metal iodides of groups I and II and may prove suitable for iodides of many other metals.

Preparation of Lithium Iodide.—Lithium iodide is prepared by the action of lithium hydride on iodine in ether solution.

$$2LiH + I_2 \xrightarrow{\text{ether}} 2LiI + H_2$$

Lithium hydride is used in excess and is readily filtered away from the lithium iodide which is very soluble in ether. The ether is pumped away leaving pure LiI.

In a typical experiment 19.0 g. (0.075 mole) of I_2 was mixed with 1.36 g. (0.17 mole) of LiH intimately in a 500-ml. three-neck flask provided with a stirrer and a dropping funnel containing 250 ml. of ether. The ether was added in small portions initially because the reaction is quite vigorous. Hydrogen was given off during the reaction and continued to be evolved until approximately 100 ml. of ether had been added. One hundred-fifty more milliliters of ether was now added and the mixture was refluxed for one hour. The mixture was filtered and the ether distilled away leaving a white salt tinged slightly yellow. After vacuum drying for one hour at 30–35°, 19.7 g. of a pure white salt was obtained for a yield of 98%.

A gravimetric iodide analysis indicated a purity of 99.0%. An analysis for lithium by passing an aqueous solution of lithium iodide through the acid form of a cation-exchange resin and titrating the acid eluted indicated a purity of 99.23%. If not properly protected from the atmosphere, lithium iodide assumes a yellowish tint and eventually becomes a deep brown.

Preparation of Barium Iodide.—An attempt to prepare barium iodide by the method developed for lithium iodide failed. It was discovered, however, that this substance could be prepared by a method equally as convenient and effective. Barium hydride reacts spontaneously with ammonium iodide in pyridine to yield barium iodide.

$$BaH_2 + 2NH_4I \xrightarrow{C_5H_5N} BaI_3 + 2NH_3 + H_2$$

Barium hydride is used in excess and is filtered away from the BaI_2 which dissolves in the pyridine, in which it is quite soluble.

In a typical experiment 12.0 g. (0.086 mole) of BaH_2 was suspended in 500 ml. of anhydrous pyridine in a 1-liter round-bottom, three-neck flask equipped with a dropping funnel and a mercury sealed stirrer; 21.87 g. (0.151 mole) of NH_4I dissolved in 125 ml. of pyridine was introduced into