(1.2), 697 (1.0), 670 (3.4), 612 (1.7), 570 (1.4), 545 (0.5), 498? (0.4), 453 (7), 419 (1.4).

Nickel Carbonyl Complex. The question whether 2-$(CF_3)_2PB_5H_8$ could form a ligand-$Ni(CO)_3$ complex without isomerization to the known 1-$(CF_3)_2PB_5H_8Ni(CO)_3$[4] was answered affirmatively by an experiment employing 0.250 mmol of nearly pure 2-$(CF_3)_2PB_5H_8$ with 0.2 ml of $Ni(CO)_4$ left together for 1 hr at 0°. The evolution of CO (0.250 mmol) began rapidly and was soon complete. The reaction occurred in a vertical tube, to the top of which was sealed an inverted nmr tube. A side arm connected the system through a horizontal ground joint to the high-vacuum line, permitting rotation for pouring the product into the nmr tube. The sealed-off nmr tube was used for four-element nmr spectra, again recorded by the Varian HA-100 instrument. Minor formation of a low-density dark brown precipitate (at the 35° probe temperature) did not interfere with the results.

The proton nmr spectrum appeared much like Figure 1, except that the major quartet was centered at 2.04 ppm downfield of TMS ($J = 174$ cps), while the asymmetric BHB peak maximized at +2.52. This obviously is different from 1-$(CF_3)_2PB_5H_8Ni(CO)_3$, for which the corresponding numbers are −2.74 ($J = 169$ cps) and +1.95 ppm.[4] The ^{19}F spectrum was a doublet at 57.0 ppm upfield of Cl_3CF ($J = 73$ cps), sharing a peak with the doublet for 1-$(CF_3)_2PB_5H_8Ni(CO)_3$ (57.8 ppm, $J = 75$ cps),[4] present as a 10% impurity. Thus, the isomeric impurity confirmed the 0.8-ppm difference of chemical shift. The ^{31}P spectrum again was only poorly recorded but could be seen as a ragged peak 15 ppm downfield of H_3PO_4. The signal:noise ratio was no greater than 3, but six repetitions of the scan left no doubt of a genuine signal.

The ^{11}B spectrum for 2-$(CF_3)_2PB_5H_8Ni(CO)_3$ was almost the same as Figure 2, but with subtly different parameters: δ_{345} 29 ± 0.5 ppm ($J = 175$ cps); δ_2 32.1 ppm; δ_1 70.0 ppm ($J = 178$ cps). Unlike the 1-isomer complex, 2-$(CF_3)_2PB_5H_8Ni(CO)_3$ failed to show B–P coupling, perhaps partly on account of superposition with the doublets belonging to the three other basal boron atoms.

Acknowledgment. This research was supported in part by Grant No. GP-17472 from the National Science Foundation.

Registry No. 1-$(CF_3)_2PB_5H_8$, 19570-53-7; 2-$(CF_3)_2PB_5H_8$, 41699-88-1; 2-$(CF_3)_2PB_5H_8Ni(CO)_3$, 41699-89-2; B_5H_9, 19624-22-7; $(CF_3)_2PCl$, 650-52-2.

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Hydrosulfides of Group I and Group II Metals

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Received July 26, 1973

A recent report by Petzel[2] prompts us to report the work going on in our laboratories on the reaction of the alkali and alkaline earth metals with hydrogen sulfide in liquid ammonia as well as the general studies on the systematic chemistry of the alkali and alkaline earth hydrosulfides and sulfides. Although the formation of the alkali and alkaline earth metal sulfides and polysulfides from the elements in liquid ammonia has been extensively studied,[3-6] the reaction system $M-H_2S$ in liquid ammonia (where M = group I or II metals) has drawn detailed attention only recently. Nelson and Lagowski[7] have suggested that the equilibrium of hydrogen sulfide in liquid ammonia to give the solvated hydrosulfide ion accounts for the formation of potassium hydrosulfide even when an excess of the metal is present in the solution. In the alkaline earth series Petzel has described good preparative methods for the sulfides starting from the reaction of hydrogen sulfide with the alkaline earth metal in liquid ammonia. Since the anhydrous hydrosulfides of the alkaline earth series have not been previously reported, our syntheses of these compounds help to resolve the seeming conflict between the observations of Lagowski and Petzel.

Experimental Section

Rubidium and cesium (99.99%, Alfa Inorganics) were separated under hard vacuum into smaller quantities (50-500 mg) in break-seal Pyrex ampoules before further use. Calcium, strontium, and barium were vacuum distilled by the method of Moyer, *et al.*[8] Hydrogen sulfide (Matheson Co.) was distilled through two traps at −80° and one at −112° and was collected at −196°. Ammonia (Matheson Co.) was degassed under vacuum at −196° and dried over sodium at −64°.

Method I. In a controlled-atmosphere glove box, the metal was dissolved in 200 ml of anhydrous ammonia in a Pyrex vessel refrigerated at −77°. Hydrogen sulfide was bubbled through the solution until the blue color discharged. The white precipitate was filtered from the solution and washed with three 150-ml portions of liquid ammonia. The product was vacuum-dried in the entry lock to the box prior to further examination.

Method II. The vessel for these reactions was designed in the shape of an "H" and was attached to a standard vacuum line. The metal was deposited in one leg; a measured amount of hydrogen sulfide was frozen into the other at −196°. Anhydrous ammonia was then condensed at −196° into both legs until about 5 ml of solution could be formed on allowing the vessel to warm to −48°. One solution was added to the other by tipping the vessel. The solutions were periodically stirred by using a glass encapsulated metal stirrer activated with a hand magnet. The hydrogen generated was collected by freezing the solutions at −196° and removing the gas with a Toepler pump. The reactions were complete when no further H_2 evolved. The stable products were removed from the vacuum line under an atmosphere of ammonia, after prior vaporization of the solvent. The unstable calcium and strontium products were degassed at −45° to remove the solvent ammonia and then warmed to room temperature with collection of the evolved gases. Hydrogen sulfide was separated from the gaseous mixture using Ascarite at −23°. Gases were analyzed using an Associated Electrical Industries MS 10 mass spectrometer.

Product handling was done in a nitrogen-flushed glove bag. All solids were characterized using Debye–Scherrer X-ray powder diffraction techniques. Thermal analyses were performed on the Du Pont 990 thermal analyzer system at typical scan times of 2–10° min^{-1} in the 0.4-mV/in. response range in a stream of pure argon.

Sulfur analyses of barium hydrosulfide hydrolyses products were determined by gravimetric methods as barium sulfate.

Results and Discussion

In work initiated some years ago[9] white precipitates were

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found to form upon mixing hydrogen sulfide with solutions of calcium, strontium, or barium metals in liquid ammonia. The recovery of the resulting precipitate at room temperatures yielded calcium and strontium monosulfides. The barium precipitate, however, was not the monosulfide, but rather the hydrosulfide. By following the hydrogen sulfide consumption during the reaction and the gas evolution on vacuum-drying of the precipitated solids, it has been shown that all the alkaline earth elements studied precipitate initially as the hydrosulfides. The calcium and strontium hydrosulfides, however, are so unstable that these products decompose when warmed to room temperature which results in the isolation of the monosulfides. It was found, however, that the hydrosulfide for both calcium and strontium could be isolated at −45°. As the hydrosulfide warmed to room temperature 1 mol of hydrogen sulfide evolved for each mole of initial hydrosulfide. The balance of the gas given off was ammonia. Four and six moles of ammonia, respectively, were found per mole of initial calcium and strontium hydrosulfide isolated at −45°. Barium hydrosulfide is the most stable of the alkaline earth hydrosulfides and was readily isolated from the reaction solution. On thermal analysis barium hydrosulfide shows one weight loss at 100° which corresponds to the loss of 1 mol of hydrogen sulfide per mole of barium hydrosulfide. There was no evidence of ammonia of crystallization. The thermal decomposition product is barium sulfide. Barium hydrosulfide prepared in this way gave a poorly resolved X-ray powder pattern showing only one broad band. Evidence for a small barium sulfide impurity was also present.

These results are consistent with previous observations. West has shown on the basis of calculated free energy changes that metal hydrosulfides are increasingly stable with increasing atomic number of the cation.[10] Nelson and Lagowski's[7] postulation of the ammoniated hydrosulfide ion would predict the precipitation of the hydrosulfides of the alkaline earths as well as the alkali metals.

The relative stabilities of the alkaline earth hydrosulfides lead one to wonder about the relative stabilities of the alkali metal hydrosulfides. Previous workers have prepared the nonsolvated hydrosulfides of all of the alkali metals by various methods.[3,11] We have also confirmed Lagowski's prediction that rubidium and cesium should form the hydrosulfides on reaction with hydrogen sulfide in liquid ammonia. The reaction stoichiometry, moles of metal to moles of hydrogen sulfide consumed and hydrogen generated, as well as the characterization of the product isolated, was used to follow the course of these latter reactions. Also as predicted the reactions of the alkali metals as well as those of the alkaline earths are independent of the order of addition of the reactant solutions, *i.e.*, whether the hydrogen sulfide solution is added to the metal solution, or *vice versa.* Reports can be found in the literature regarding the stability of the hydrosulfides of lithium, sodium, and potassium. The alkali metal hydrosulfide predicted to be the least stable, LiSH, decomposes to the sulfide at 150° under vacuum.[11] Sodium hydrosulfide decomposes under vacuum at a fairly rapid rate at 250° but must be heated subsequently to 500° to convert it completely to the monosulfide.[12] In air or in an inert atmosphere it forms a colored material, the color being attributed to polysulfide formation. Bloxam[13] in an earlier report stated that potassium hydrosulfide is stable toward heat. This is not surprising in view of our results on rubidium hydrosulfide. Thermogravimetric analysis in an argon atmosphere shows that rubidium hydrosulfide decomposes at 505° yielding only 0.07 mol of hydrogen sulfide per mole of rubidium hydrosulfide. When heated under vacuum, rubidium hydrosulfide exhibits a measurable pressure at 430°. The yellow solid which results on heating to 450° is shown by its X-ray diffraction powder pattern to be essentially rubidium hydrosulfide. Cesium hydrosulfide was found to behave qualitatively like rubidium hydrosulfide. The cesium hydrosulfide produced a measurable pressure and turned yellow below 370–380° on vacuum heating. The small weight loss accompanying these decompositions suggests that the colored residues obtained from the rubidium hydrosulfide and cesium hydrosulfide are mixtures consisting of the starting material and some polysulfides. Unlike the lighter members of the series, the rubidium and cesium hydrosulfides do not form monosulfides on heating. Another aspect of the relative stabilities of the hydrosulfides and sulfides is demonstrated by the stability of the sulfides in liquid ammonia. All of the sulfides from lithium to rubidium are stable in liquid ammonia.[5,6] However, cesium sulfide undergoes solvolysis in liquid ammonia to form cesium hydrosulfide and cesium amide.[14]

The hydrolyses of the hydrosulfides of rubidium, cesium, strontium, and barium were studied. All undergo rapid hydrolysis in moist air evolving hydrogen sulfide. Barium hydrosulfide on exposure to air forms barium carbonate by first hydrolyzing and then reacting with the carbon dioxide in the air. Complete hydrolysis of barium hydrosulfide in a stream of moist nitrogen formed $Ba(OH)(SH)\cdot 2.6H_2O$ which is similar to the formula $Ba(OH)(SH)\cdot 3H_2O$ found by earlier workers.[15] When the hydrolysis was performed under static conditions on a vacuum line, the vacuum-dried product corresponded to the formula $Ba(OH)_x(SH)_{2-x}\cdot H_2O$ where $x \leq 1$. The hydrolysis was found to cease after a pressure of 2 mm of hydrogen sulfide accumulated above the product. Continual removal of hydrogen sulfide allowed complete conversion to the hydroxyhydrosulfide. The barium hydroxyhydrosulfide hydrate lost water and some hydrogen sulfide when heated to 50°, where they formed a stable barium sulfide rich (~70%) residue.

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