497. *Sodium Derivatives of Stannane.*

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Conductometric titration of a solution of sodium in liquid ammonia with stannane shows the formation of stannylsodium (sodiostannane), SnH_3Na, and stannylenedisodium (disodiostannane), SnH_2Na_2. The former decomposes at $-63{\cdot}5°$ in absence of ammonia, but reacts in ammonia solution with alkyl iodides to form alkyl stannanes, and with ammonium chloride to form stannane. Stannylenedisodium is fairly stable at 0° in absence of ammonia. In ammonia solution it does not react with methyl iodide and, with ammonium chloride, gives stannane. An attempt to prepare plumbane, PbH_4, by the reduction of lead tetrachloride with lithium aluminium hydride yielded only metallic lead.

Sodium derivatives of alkyl- and aryl-tin hydrides are formed by the reaction of sodium in liquid ammonia solution with organotin mono- and di-halides, or with the corresponding hydrides. The stability appears to be greatest with three alkyl or aryl groups in the molecule. Thus, both trimethyl- and triphenyl-stannylsodium are known in the solid state.[1] Dimethylstannylsodium is unknown and dimethylstannylenedisodium is known only as its deep red solution in liquid ammonia.[2] There has been no systematic search for compounds of the type $RSnH_2Na$ and SnH_3Na, notwithstanding the isolation of germanylsodium, GeH_3Na, as an ammine and the probable existence in ammonia solution of germanylenedisodium, GeH_2Na_2.[3] The ready decomposition of stannane at room temperature made it probable that stannylsodium, SnH_3Na, would, if it existed, be very unstable. Evidence for its existence was therefore sought by the conductometric titration with stannane of a solution of sodium in liquid ammonia. This method allowed the existence of one or more sodium derivatives at relatively low temperatures to be examined.

In a study of its kinetics, which will be published elsewhere, the decomposition of the gas was found to be completely inhibited by a small proportion of oxygen, which probably poisoned the tin surface on which the hydride is known to decompose catalytically. This finding greatly facilitated both the preparation and storage of stannane. The hydride also decomposed readily in presence of gaseous ammonia, so additions of stannane to ammonia solutions were made at low temperatures. Conductivity measurements were made at $-63{\cdot}5°$ (m. p. of chloroform) in a cell of conventional design. This was charged

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[1] Kraus and Sessions, *J. Amer. Chem. Soc.*, 1925, **47**, 2361; Chambers and Scherer, *ibid.*, 1926, **48**, 1054.

[2] Kraus and Kahler, *ibid.*, 1933, **55**, 3537; Kraus and Johnson, *ibid.*, 1933, **55**, 3542.

[3] Kraus and Carney, *ibid.*, 1934, **56**, 765.

with a solution of sodium in ammonia, the conductivity of which was measured. Small successive additions of stannane were then made at liquid-nitrogen temperature and reaction was allowed to occur at —63·5°. The conductivity and hydrogen evolved were measured after each addition.

The typical titration curve (Fig. 1) was obtained with 0·0113 g. of sodium in 5·590 g. of ammonia. At the minimum, which occurred when about 70% of stannane needed to form stannylsodium had been added, the blue colour of the solution had just disappeared. Since the minimum occurred at a lower hydride : sodium ratio than unity, we concluded that at this stage some of the sodium was present as stannylenedisodium, SnH_2Na_2, which later reacted with fresh stannane to form stannylsodium. When enough stannane had been added to give a ratio of reactants of just above unity the conductivity became constant and only stannylsodium was present. This was borne out by measurement of the hydrogen evolved in the thermal decomposition of the end product after the removal of ammonia. It corresponded in amount with the decomposition of H_3SnNa. The initial sodium solution had an equivalent conductivity of 786 ohm^{-1} $cm.^{-1}$, and the stannylsodium solution had the high value of 372 ohm^{-1} $cm.^{-1}$.

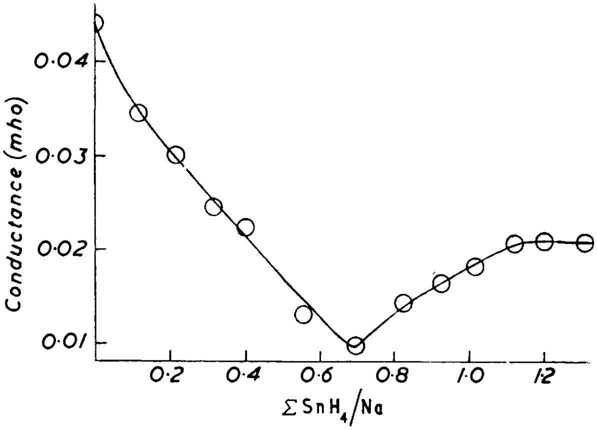

FIG. 1. *Conductometric titration of a solution of sodium in liquid ammonia with gaseous stannane.*

The hydrogen evolution as a function of the mole-fraction of stannane added is shown in Fig. 2. The ratio of total hydrogen evolved to total stannane added (ordinate) would have a value of 1·0 for the formation of H_2SnNa_2 and of 0·5 for H_3SnNa. The curve is consistent with the initial formation of the former, and its gradual transformation into the latter. The final value for the hydrogen evolution is 0·55 and not 0·5 owing to a little decomposition of stannane to tin and hydrogen in the later stages of the titration, when no free sodium was present. The tin was deposited as a mirror above the level of the ammonia solution. The direct formation of sodamide from sodium and ammonia is unlikely since both stannylsodium and stannylenedisodium can be formed quantitatively under suitable conditions and characterised by the hydrogen evolved in their decompositions. It was shown in preliminary experiments that the reaction $H_3SnNa + Na = H_2SnNa_2 + \frac{1}{2}H_2$ occurs very slowly at —63·5°, as does the corresponding reaction of germanylsodium. Even after 10 hr. the conversion of 0·0876 g. of stannylsodium into stannylenedisodium by a two-fold excess of sodium was only 30% complete.

Stannylenedisodium was prepared by reaction of a tenfold excess of sodium with stannane in ammonia at —63·5°. Excess of sodium was removed by reaction with ethyl chloride, which did not react with stannylenedisodium. Decomposition of the ammonia-free compound was not appreciable until 0° but at 15° was complete in half an hour, hydrogen evolution being in accord with the equation $H_2SnNa_2 = SnNa_2 + H_2$. After removal of sodium, stannylenedisodium did not react with methyl iodide in ammonia and the hydrogen evolved in its subsequent decomposition at room temperature after removal of ammonia was equimolar with the amount of stannane used in the preparation. Stannylsodium was less stable and decomposed at $-63\cdot5°$ as soon as ammonia was removed. The hydrogen evolved was in accord with the equation $H_3SnNa = SnNa + \frac{3}{2}H_2$. It is probable that stannylsodium, like germanylsodium,[3] is stable only as an ammine.

Stannylsodium reacted with alkyl iodides at $-63\cdot5°$ in ammonia solution to form alkylstannanes and sodium iodide. Methyl-, ethyl-, and *n*-propyl-stannanes were so prepared. Their stability decreased with increase in the molecular weight of the organic radical and, in the case of the *n*-propyl derivative, was so low at room temperature that the yield was poor. This type of reaction is also found for germanylsodium.[4] Stannylsodium, like germanylsodium, did not react with methylene chloride.

Organostannanes were first made by the action of an ammonium halide in liquid ammonia on the appropriate organostannylsodium. In this way, trimethyl-, triphenyl-, and diphenyl-stannane were prepared.[5] Monogermane can also be similarly regenerated from germanylsodium [3] and it has been shown that both stannylsodium and stannylenedisodium also react in this way with a solution of ammonium chloride in ammonia at $-63\cdot5°$:

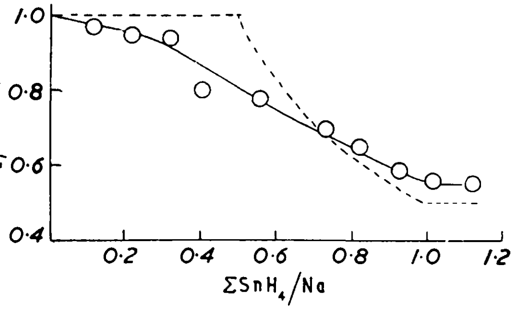

FIG. 2. *Hydrogen evolution during the titration of a solution of sodium in liquid ammonia with gaseous stannane.*

The broken line shows the hydrogen evolution expected if stannylenedisodium had been first formed and later converted into stannylsodium.

$$H_3SnNa + NH_4Cl = SnH_4 + NaCl + NH_3$$

$$H_2SnNa_2 + 2NH_4Cl = SnH_4 + 2NaCl + 2NH_3$$

The high yield of stannane obtained in the reduction of stannic chloride by lithium aluminium hydride (80—90% based on $LiAlH_4$, according to $SnCl_4 + 4LiAlH_4 = SnH_4 + 4LiCl + 4AlH_3$) suggested that plumbane, PbH_4, might be similarly obtained from plumbic chloride. At $-78°$ plumbic chloride and lithium aluminium hydride reacted in ether to give metallic lead.

Three claims to the preparation of plumbane have been made,[7] although all have been criticised.[8] Piper and Wilson failed to prepare plumbane by the reduction of plumbous chloride with sodium borohydride, although this method gives good yields of germane [9] and stannane.[10] Plumbane probably does not exist as a stable compound, although it may be formed as a reaction intermediate, *e.g.*, in the reduction of plumbic chloride by lithium aluminium hydride.

EXPERIMENTAL

Stannane was prepared by a modification of Finholt and Schlesinger's method.[6] An ether slurry of the solid ether adduct of stannic chloride was put in the reaction vessel and frozen

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[4] Teal and Kraus, *J. Amer. Chem. Soc.*, 1950, **72**, 4706; Kraus and Carney, *ibid.*, 1934, **56**, 765.

[5] Kraus and Greer, *ibid.*, 1922, **44**, 2629; Chambers and Scherer, *ibid.*, 1926, **48**, 1054.

[6] Finholt, Schlesinger, Wilzbach, and Bond, *ibid.*, 1947, **69**, 2692.

[7] Paneth and Nörring, *Ber.*, 1920, **53**, 1693; Schultze and Müller, *Z. phys. Chem.*, 1930. *B*, **6**, 267; Weeks, *J.*, 1925, **127**, 2845.

[8] See, for example, Pearson, Robinson, and Stoddart, *Proc. Roy. Soc.*, 1933, *A*, **142**. 275; Hurd, "Chemistry of the Hydrides," 1952, p. 118.

[9] Piper and Wilson, *J. Inorg. Nuclear Chem.*, 1957, **4**, 22.

[10] Schaeffer and Emilius, *J. Amer. Chem. Soc.*, 1954, **76**, 1203.

in liquid nitrogen. An ether solution of lithium aluminium hydride was added and frozen. A stream of nitrogen containing 0·1% of oxygen to inhibit the decomposition of the stannane was passed and the reaction vessel was warmed to −78° until the ether was liquid and then to −63·5° until the solution was brown. The temperature was allowed to increase gradually (1 hr.) to −20°, and evolution of stannane was then complete. The gas was collected in a trap cooled in liquid nitrogen and purified by repeated passage through a trap cooled to −112°, which condensed traces of ether and allowed stannane to pass. Purity was checked by molecular-weight and vapour-pressure measurements. The stannane was stored as gas at room temperature with about 10% of oxygen from which it was freed as required by condensation. In a typical run 22·3 g. of ether adduct and 10 g. of lithium aluminium hydride gave 6·7 g. of pure stannane.

The conductivity cell was cylindrical (1·7 cm. diam., 20 cm. long), with two blackened platinum electrodes, each of 1 cm.^{2} area, held in long glass leads. The cell constant was 1·75. It was connected by a tap and standard joint to a vacuum fractionation apparatus. The solution of sodium in liquid ammonia was prepared by rapidly weighing a piece of freshly-cut reagent grade sodium (*ca.* 0·01 g.), putting it in the cell and evacuating. Ammonia (*ca.* 2 ml.), dried over sodium, was condensed into the cell and kept for 30 min. at −63·5° to obtain a homogeneous solution. No hydrogen was evolved. The conductivity was measured at −63·5°. About one-tenth of the stannane required to give a SnH_4 : Na ratio of unity was weighed as gas and condensed into the cell by cooling it in liquid nitrogen. It was allowed to react with sodium at −63·5° for 15 min., and the conductivity and hydrogen evolved were then measured. This was repeated after successive additions of stannane up to a 1 : 1 ratio. At the end of the run the ammonia was removed and weighed.

Preparation and Properties of Stannylsodium.—Sodium (0·0145 g.) was dissolved in ammonia (~3 g.) in a reaction tube attached to the vacuum apparatus. The solution was frozen in liquid nitrogen and stannane (0·0824 g.) condensed in. After ½ hr. at −63·5° hydrogen was pumped off and measured by volume (Found: H, 0·000654 g. Calc. for reaction to form H_3SnNa: H, 0·000634 g.). Ammonia was pumped off at −63·5°. As the last of the solvent was removed the solution became black and hydrogen was evolved slowly. Decomposition was rapid at 0°. The total hydrogen was measured (Found: H, 0·00196 g. Calc. for decomposition of 0·0916 g. of H_3SnNa: H, 0·00192 g.). The black solid residue gave hydrogen and an alkaline solution on addition of water, forming a black solid which gave the *X*-ray pattern of white tin. In a second experiment decomposition of stannylsodium was rapid at 0°, even in presence of a 40 cm. pressure of ammonia. There was no evidence that an ammine was formed.

Reactions of Stannylsodium.—(a) *With methyl iodide.* Methyl iodide (0·1 g.) was condensed on a frozen solution of stannylsodium (0·117 g.) in ammonia, prepared as above. There was an immediate white precipitate on warming to −63·5°. After 5 min. volatile products were washed with a solution of copper sulphate in 10% sulphuric acid to remove ammonia. The decomposition of the methylstannane, which would otherwise have been catalysed by the ammonia, was inhibited by the oxygen dissolved in the solution. The residual volatile material was dried by passage through a trap at −95°. The product was methylstannane (0·100 g.; yield 94% on stannane taken), b. p. 1·4° (extrapolated) (lit.,[6] 0°) (Found: *M*, 137. Calc. for CH_6Sn: *M*, 137). The infrared spectrum was identical with that of a specimen made by reducing methyltrichlorostannane with lithium aluminium hydride, having the following peaks: 3692 (w), 3000 (m), 2932 (m), 2835 (w), 1875 (v.s.) broad, 1751 (w), 1583 (w), 1464 (w), 1265 (w), 1145 (w), 700 (s), 680 cm.$^{-1}$ (s).

(b) *With ethyl iodide.* The above procedure was used (stannylsodium, 0·101 g.; ethyl iodide, 0·08 g.). The product, dried by passage as vapour through a trap at −78°, was *ethylstannane* (0·036 g.), b. p. 25° (extrapolated) (Found: *M*, 151. C_2H_8Sn requires *M*, 151). The infrared spectrum showed the following peaks: 2940 (m), 1869 (v.s.), 1470 (w), 1382 (w), 1208 (w), 1195 (w), 1020 (w), 686 (v.s.), 674 cm.$^{-1}$ (s). The compound decomposed slowly at room temperature.

(c) *With* n-*propyl iodide.* Using the same procedure (stannylsodium, 0·0982 g.; *n*-propyl iodide, 0·07 g.), and removing water at −63·5°, we obtained n-*propylstannane* (0·0458 g.) (Found: *M*, 165. $C_3H_{10}Sn$ requires *M*, 165). It decomposed before either its infrared spectrum or vapour-pressure curve could be obtained.

(d) *With ammonium chloride.* Ammonium chloride (~2·5 g.) was added slowly by a rotating arm to a solution of stannylsodium (0·111 g.) in liquid ammonia at $-63·5°$. Stannane (0·0613 g., 80%) was evolved (Found: *M*, 122. Calc. for H_4Sn: *M*, 123) and separated from ammonia as described above. The infrared spectrum was identical with that of stannane.

Preparation and Properties of Stannylenedisodium.—The same method was used as for stannylsodium with stannane (0·0530 g.) and a ten-fold excess of sodium (0·12 g.). The hydrogen evolved was 0·001064 g. (Calc. for complete conversion into H_2SnNa_2: 0·001060 g.). When only a two-fold excess of sodium was used the hydrogen evolved corresponded with a mixture of H_3SnNa (~10%) and H_2SnNa_2 (~90%). Excess of sodium was removed by adding ethyl chloride (0·5 g.) to the frozen ammonia solution of stannylsodium, allowing it to react at $-63·5°$ (10 min.) and pumping off excess of ethyl chloride and solvent ammonia at $-63·5°$. Fresh ammonia was then condensed into the reaction vessel.

Stannylenedisodium did not decompose when ammonia was removed at $-63·5°$. When the temperature was raised gradually (5 hr.) to $-20°$, hydrogen evolution showed 3% decomposition. Decomposition was complete in 30 min. at 15°, 0·0883 g. (0·000530 mole) of H_2SnNa_2 giving 0·00105 g. (0·000525 mole) of hydrogen. The black decomposition residue reacted with water with a yellow flash, hydrogen evolution and formation of a residue with the *X*-ray pattern of white tin.

Reactions of Stannylenedisodium.—(a) *With ethyl chloride and methyl iodide.* Excess of ethyl chloride (1·0 g.) was added to a solution of stannylenedisodium (0·204 g.) in liquid ammonia from which excess of sodium had not been removed. There was immediate reaction at $-63·5°$ between sodium and ethyl chloride. After ½ hr. ammonia was removed chemically as before and the volatile residue passed through a trap at $-95°$ to condense diethylstannane and water. The condensate showed no trace in its infrared spectrum of the very strong Sn–H stretching frequency at 1875 cm.$^{-1}$. The residue in the reaction vessel decomposed on warming and evolved 0·0244 g. of hydrogen (Calc. for 0·204 g. of H_2SnNa_2: 0·0245 g.). With stannylenedisodium (0·133 g.) from which excess of sodium had been removed with ethyl chloride, there was no evidence for the formation of a methylstannane on treatment as before with methyl iodide (0·217 g.). After removal of all volatile products thermal decomposition of the residue gave 0·00186 g. of hydrogen (Calc. for 0·133 g. of H_2SnNa_2: 0·00184 g.).

(b) *With ammonium chloride.* Stannylenedisodium (0·169 g.) with ammonium chloride (~2·5 g.) in ammonia solution gave 0·0812 g. of stannane (theoretical 0·124 g.). The infrared spectrum was identical with that of stannane.

Attempted Preparation of Plumbane.—An attempt was made to prepare plumbane by the reduction of plumbic chloride with lithium aluminium hydride. The apparatus was that used for the preparation of stannane. The ether adduct of 10 g. of plumbic chloride was made and quickly frozen in the reaction vessel. After addition and freezing of a mixture of ether and solid lithium aluminium hydride (8 g.) the reaction vessel was warmed, first to $-96°$ and then, when the ether had liquefied, to $-78°$. At this temperature the plumbic chloride was slowly reduced to a black powder which *X*-ray powder photography showed to be metallic lead. Throughout the preparation nitrogen was bubbled through the solution, the volatile products being collected in liquid-nitrogen traps. At the end of the reaction the material in these traps was found to be completely condensed in a trap cooled to $-95°$. The condensate was ether [Found: *M*, 73·5. Calc. for $(C_2H_5)_2O$: *M*, 74·0], its infrared spectrum had no adsorption in addition to that expected for ether, and no metallic mirror was formed on standing at room temperature.

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