REDUCTION OF TRIMETHYL STANNYL HYDROXIDE IN LIQUID AMMONIA.

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The alkali metals are very strong reducing agents. Fittig and Wurtz have applied this principle in the synthesis of various hydrocarbons at ordinary temperatures in ethereal solutions ; however, the rate of reaction is very slow, It has been recognized that the alkali metals, such as sodium and potassium, in liquid ammonia solution react as strong and convenient reducing agents for various organic compounds and possess the advantage that the reduction may be carried out at as low a temperature as 33.5° C. Therefore, in such a solution, the stability of the resulting substance is relatively great. The reactions involved are in many cases instanteneous and quantitative.

Metallic sodium is extremely soluble in liquid ammonia in which the following reactions probably take place :(1)

$$\begin{array}{l} \mathrm{Na}+\mathrm{NH_3} \rightleftarrows [\mathrm{NaNH_3}^+ + e^-] \rightleftarrows \mathrm{Na} + e^- + \mathrm{NH_3} \\ \qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\quad \mathrm{NaNH_2} + \mathrm{H}^+ + e^- \rightarrow \mathrm{NaNH_2} + \tfrac{1}{2}\mathrm{H_2} \end{array}$$

It is interesting to note that the characteristic blue color reaction is present even with a minute trace of sodium in the solution. In the above reaction, the formation of $NaNH_2$ and H_2 is very slow in comparison with others.

The reactions of alkali metals on organic compounds in liquid ammonia were first investigated by Moissan.(2) Since then it has been extensively developed by Lebeau(3), Lebeau and Picon(4), Kraus(5), Kraus and his students(6),

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(1) Kraus *J. Am. Chem. Soc.*, **30** (1908), 1323.

(2) *Compt. rend.*, **127** (1898), 911 ; **136,** (1903), 1217.

(3) Lebeau, ibid., **140** (1905), 1042, 1264.

(4) Lebeau and Picon, ibid., **157** (1913), 137,223 ; **158** (1914), 1514 ; **159** (1914), 70 ; **173** (1921), 84 ; Picon, ibid., **175** (1922), 1213 ; Picon, *Bull. soc. chim.*, **35** (1924), 979.

(5) Kraus, *J. Am. Chem. Soc.*, **35** (1913), 1732.

(6) Kraus and Greer, *J. Am. Chem. Soc.*, **44** (1922), 2629 ; Kraus and White, ibid., **45** (1923), 768 ; Kraus and Kawamura, ibid., **45** (1923), 2756 ; Kraus and Sessions, ibid., **47** (1925), 2361 ; Kraus and Bullard, ibid., **48** (1926), 2131 ; Kraus and Rosen, ibid., **47** (1925), 2739 ; Kraus and Foster, ibid., **49** (1927), 457 ; Kraus and Neal, ibid., **51** (1929), 2403.

Chablay(1), Dains, Vaughan and Janney(2), Clifford(3), White(4), and White and his students(5). Other workers will be found elsewhere. X denotes an electro-negative radical or element and R an electro-positive radical or element. Since various salts, acids and bases assume a state of more or less electrical dissociation in liquid ammonia (a condition which does not necessarily require the actual solution of these materials), they may be represented according to the following general equation:

$$RX = R^+ + X^-$$

The reactions between organic compounds and alkali metals in liquid ammonia are extremely varied and quite complex. This is shown by Professors Kraus and White, and with their students, on a large number of experiments with various organic compounds. It has been stated that organic compounds containing strong electro-negative radicals or elements are, in general, reduced to the radical or elements of the radical, forming salts with the reducing metals, depending upon the nature of the radical in question and various other substances present. For instance, an alkyl or aryl radical is relatively strongly electro-positive and weakly electro-negative and univalent. Since the sodium salt of these groups is very unstable in liquid ammonia, it hydrolyzes (ammonolyzes) to form its hydrocarbon and amines(6). In such an electro-negative radical, the electron is relatively loosely attached to the radical and therefore tends to combine with a more strongly electro-negative radical or element; while in the case of $(C_6H_5)_3CK$(7) or $(CH_3)_3SnNa$(8) the electron is relatively strongly or moderately strongly attached to the radical since they are not ammonolyzed in liquid ammonia solution. However the latter hydrolyzes in the presence of ammonium chloride to form trimethyl stannane, $(CH_3)_3SnH$(9).

The general reactions may be represented as follows:

$$\text{I} \qquad R^+ + X^- + Na^+ + e^- = R + Na^+X^-$$

$$\text{II} \qquad R^+ + X^- + 2Na^+ + 2e^- = R^-Na^+ + Na^+X^-$$

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(1) *Compt. rend.*, **140** (1905), 1262; **154** (1912), 364; **156** (1913), 1020; *Ann. Chim.*, **9.** I, (1914), 469.

(2) *J. Am. Chem. Soc.*, **40** (1918), 936.

(3) ibid., **41** (1919), 1051.

(4) ibid., **45** (1923), 779.

(5) White and Knight, ibid., **45** (1923), 1781; White, Morrison and Anderson, ibid., **46** (1924), 961; Wooster, **50**, (1928), 1388.

(6) White, *J. Am. Chem. Soc.*, **45** (1923), 779.

(7) Kraus and Rosen, *J. Am. Chem. Soc.*, **47** (1925), 2739.

(8) Kraus and Sessions, ibid., **47** (1925), 2361.

(9) Kraus and Greer, ibid., **44** (1922), 2629.

A couple of years ago, the author prepared trimethyl stannyl free radical⑴ by the reduction of trimethyl stannyl hydroxide as one of the materials for the preparation or the reduction products of the so-called "Metallo Organic Oxonium Salt," $[(CH_3)_3Sn]_2O(CH_3)_3SnX$, with metallic sodium in liquid ammonia. The present paper will describe its method of preparation in some detail.

Apparatus. The reaction tube A is immersed in a Dewer tube B containing commercial liquid ammonia as shown in the accompanying figure.

Dewer tube B has a capacity of about 700 c.c. It is 45 cm. long, and 5.5 cm. in diameter. Ammonia dried by sodium is introduced into the reaction tube through the inlet tube C. The side tube D permits the introduction of air, oxygen or nitrogen gas, at will. The reaction tube is connected through the pinchcock F with the mercury manometer H, in which the pressure can be varied at G, as desired. The reaction tube also has a side tube J, with rubber stopper K, through which small pieces of alkali metal can be introduced into the reaction tube. The tube L with stop cock M is connected with the side tube E of the reaction tube, and by this means, ammonia and other accompanying gases can be drawn out from the manometer outlet and can be collected over the water in the burette W which is filled with water from the vessel P by suction through the stop cock O.

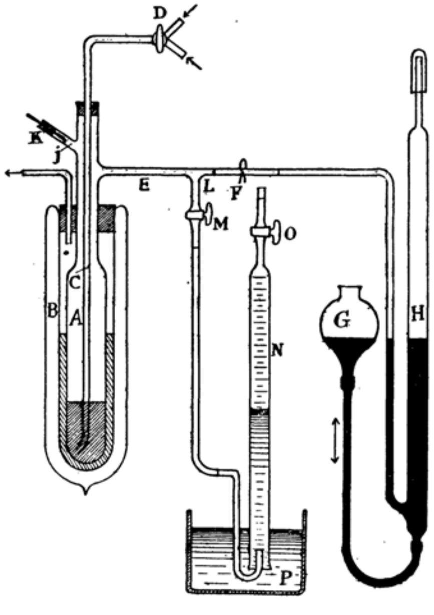

Fig. 1.

Preparation of Trimethyl Stannyl Iodide. Trimethyltin iodide was prepared by treating sodium-tin or sodium-tin-zinc alloy with methyl iodide.⑵

The alloys were treated over night with methyl iodide at room temperature and then heated on a water bath and finally in an oil bath at 120°C. The products then were separated by means of fractional distillation.

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(1) This Bulletin, **2** (1927), 107.

(2) Tetramethyl tin by Cahours, *Ann.*, **111** (1859), 236 and Ladenburg, *Ann. Suppl.*, **8** (1870), 74.

Zn%	Na%	Sn%	Alloy	CH_3I	$(CH_3)_3SnI$	$(CH_3)_4Sn$
2	14	C.P. 84	128	97	trace	22.8
-	7	C.P. 93	45	35	5	-
0.5	7	Comm. 92.5	115	90	41	2
-	14	Comm. 86	92	70	trace	16

The results indicate that the amount of sodium in the alloy is a controlling factor in regard to the production of $(CH_3)_3SnI$ or $(CH_3)_4Sn$, whereas zinc is more in the nature of a catalyzer of the reaction. This material also may be obtained by treating tetramethyl tin with iodine in a bath of ice water according to the following reaction equation:

$$(CH_3)_4Sn + I_2 = (CH_3)_3SnI + CH_3I$$

Trimethyl Stannyl Hydroxide. This compound was prepared by treating trimethyltin iodide with concentrated sodium hydroxide in alcoholic solution and distilled.

$$(CH_3)_3SnI + NaOH = (CH_3)_3SnOH + NaI$$

When the alcoholic solution is evaporated under suitable conditions it gives colorless crystals. On heating, it sublimes in a white, snow-like form. It can be recrystallized out from strong alcoholic solution as large colorless crystals. It melts and sublimes at 118°C.

Trimethyl Stannyl free Radical. One molecular proportion of trimethyltin hydroxide was dissolved in liquid ammonia by passing a stream of ammonia through the clear solution and then one atomic proportion of small pieces of sodium was added slowly. Sodium reacted readily with the hydroxide without an evolution of gas along with the addition of sodium, and a white precipitate was formed and settled in the bottom of the reaction tube. When the total amount of sodium had been added to the solution, the ammonia was evaporated at room temperature and the resulting product was treated with alcohol and washed with an excess of water until free from sodium hydroxide. The yield was quantitative. The trimethyltin free radical thus obtained may be separated as a heavy, oily liquid by a separatory funnel through filter paper with anhydrous sodium sulphate in an atmosphere of nitrogen. It melts at 23°C. and boils at 181°C. and is not appreciably soluble in water.

Anal. Subst. $=0.5241$gr.; $SnO_2=0.4840$gr. Found: $Sn=72.60\%$. Calc. for $(CH_3)_3Sn$: $Sn=72.46\%$.

The compound was entirely identical with which obtained from trimethyltin halide with sodium in liquid ammonia by Kraus and Sessions(1).

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(1) Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2361.

The free radical possesses strong reducing power. It reduces silver nitrate in solution into metallic silver instantly.

$$(CH_3)_3Sn + Ag^+ + NO_3^- = Ag + (CH_3)_3Sn^+NO_3^-$$

Kraus and Sessions show the molecular weight of the radical in benzene at boiling point, at lower concentration, to be monomolecular; and at higher concentration to be dimolecular in form. However even at low concentration at its freezing point it is completely polymerized to the stanno-ethane⁽¹⁾:

$$2(CH_3)_3Sn \overset{\text{benzene}}{\rightleftarrows} [(CH_3)_3Sn]_2$$

when trimethyltin free group is treated with one atomic proportion of sodium in the solution it forms the corresponding sodium salt:

$$(CH_3)_3Sn + Na^+ + e^- = (CH_3)_3Sn^-Na^+$$

which is soluble and a light yellow color in liquid ammonia. According to Kraus and Sessions it is a good conductor in the solution. When an equivalent trimethyltin iodide was added to the resulting trimethyltin sodium the free group again settled to the bottom of the tube. In concluding, trimethyltin hydroxide is a fairly strong base since it ionizes to form $(CH_3)_3Sn^+$ and OH^- in liquid ammonia solution. The positive ion group $(CH_3)_3Sn^+$ is reduced by the electron into the neutral $(CH_3)_3Sn$ which is insoluble in the solution. However, along with the addition of an excess of sodium, the group dissolves in the solution again, for the group becomes electrically charged, due to the electron, forming the salt of $(CH_3)_3SnNa$.

Summary.

(1) General method of reduction of compounds in liquid ammonia by alkali metals and apparatus were described.

(2) Trimethyl stannyl iodide from methyl iodide and sodium-tin alloy and from which trimethyl stannyl hydroxide was prepared.

(3) Trimethyl stannyl free radical was prepared by the reduction of trimethyl stannyl hydroxide with metallic sodium in liquid ammonia solution.

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(1) Kraus and Bullard, *J. Am. Chem. Soc.*, **48** (1926), 2131.