evolved and heats of reaction (ΔH) as heat *absorbed* by the system

$$Q_u = 2Q_{CH_2} - Q_{H_2} - \Delta H_{hyd.}$$

where $\Delta H_{hyd.}$ is the heat of hydrogenation of the polymer per structural unit —(CH═CH) —, and Q_u, Q_{CH_2} and Q_{H_2} are the respective heats of combustion of the polymer per structural unit, of the hydrogenated polymer per —CH_2— group, and of hydrogen. If the hydrogenation of the polymer is imagined to proceed by the hydrogenation of consecutive structural units, the hydrogenation of one unit is seen to be analogous to the partial hydrogenation of 1,3-butadiene to *n*-butene-1, for which $\Delta H_{hyd.} = -26.72$ kcal. per mole.[3] However, allowance should be made for the presence of the saturated substituent (previously hydrogenated) on the one carbon atom of the structural unit undergoing hydrogenation. Although heats of hydrogenation of compounds of the type CH_2═CH—CH═CH—R have not been determined, Kistiakowsky and co-workers[4] have shown that monoalkyl substitution of an α-mono-olefin reduces the magnitude of $\Delta H_{hyd.}$ by about 2 kcal. Hence, the best value for $\Delta H_{hyd.}$ is approximately -25 kcal. Rossini,[5] from heats of combustion of gaseous hydrocarbons, has shown that $Q_{CH_2} = 157.0$ kcal. Taking $Q_{H_2} = 68.3$ kcal.,[5] one obtains for the combustion of the gaseous polymer $Q_u = 271$ kcal. Assuming about 4 kcal. for the heat of sublimation per structural unit, the heat of combustion of solid polymer becomes 267 kcal. per structural unit. This excellent agreement with Lind and Schiflett's experimental value for the heat of combustion of cuprene substantiates the structure assumed above.

Using 311 kcal. for the heat of combustion of acetylene,[6] Lind and Schiflett's experimental heat of combustion of solid cuprene leads to -46 kcal. for ΔH_p, the heat of polymerization of acetylene to cuprene; the calculated heat of combustion of solid cuprene leads to $\Delta H_p = -44$ kcal.; for the formation of gaseous cuprene ΔH_p (calcd.) $= -40$ kcal. In comparison, ΔH_p for the formation of gaseous linear polymers from gaseous ethylene or higher olefins is -23 kcal.[7]

WILMINGTON, DELAWARE RECEIVED MARCH 29, 1937

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[3] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

[4] *Ibid.*, **57**, 876 (1935); *ibid.*, **58**, 137 (1936).

[5] F. D. Rossini, *Bur. Standards J. Research*, **13**, 21 (1934).

[6] F. R. Bichowsky and F. D. Rossini, "The Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York, 1936.

[7] Flory, THIS JOURNAL, **59**, 241 (1937).

Reduction of Nitroguanidine. VIII
The Formation of Aminoguanidine by Reduction in Liquid Ammonia Solution[1]

BY LAURENCE P. FULLER, EUGENE LIEBER AND G. B. L. SMITH

The study of the reduction of nitroguanidine in liquid ammonia solution with active metals is unrecorded. This note presents the results of the preliminary study of the behavior of nitro- and nitrosoguanidine in that medium, and describes the conditions necessary for the formation of aminoguanidine by their reduction with metallic sodium.

In contrast to their very low solubility in water and the usual organic solvents, nitro- and nitrosoguanidine were found to be very soluble in liquid ammonia, the latter forming a bright yellow solution. Either can be recovered unchanged by evaporation of the solvent. Addition of either nitro- or nitrosoguanidine to a solution of sodium amide in liquid ammonia causes no visible precipitation of a sodium derivative, and after the evaporation of the solvent the nitro- and nitrosoguanidine can be recovered unchanged. The addition of metallic sodium to a liquid ammonia solution of nitroguanidine produces an extremely vigorous reaction, the sodium undergoing very rapid dissolution. As sodium was added in successive portions to colorless solutions of nitroguanidine in liquid ammonia, a series of color changes and precipitations was obtained which paralleled exactly the reduction of nitrobenzene in liquid ammonia with sodium, as observed by White and Knight.[2] The solutions became yellow, then orange, reddish-orange and finally a murky brownish-orange, while a precipitate which at first is white, gradually darkens as the reduction proceeds. The return of the sodium blue color was taken as the end-point of the reduction.

The formation of nitrosoguanidine from nitroguanidine theoretically requires two atoms of sodium and when this amount of sodium was employed a yellow solution was produced. However, no nitrosoguanidine was obtained. On further addition of sodium, the blue color was always obtained before the six atoms of sodium, theoretically required for the formation of aminoguanidine, could be added. The molar ratios of

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[1] For more full details see M. S. Thesis by Laurence P. Fuller, Polytechnic Institute of Brooklyn, 1937. Contribution No. 33 from the Department of Chemistry of the Polytechnic Institute of Brooklyn.

[2] White and Knight, THIS JOURNAL, **45**, 1780 (1923).

sodium to nitroguanidine which were obtained to the blue color end-point varied from 3.7:1 to 4.5:1[3] depending on the quantity of the nitroguanidine taken. The residues obtained on evaporation of the ammonia contained no aminoguanidine. Cyanamide was definitely identified to the extent of 10%. Found, %Ag, 83.15; calculated for CN_2Ag_2, %Ag, 84.36. By treatment of the silver derivative with hydrogen sulfide, hygroscopic crystals of melting point 39.5°[4] were obtained.

During the reductions a vigorous evolution of gas takes place. Examination of the gas showed it to be pure nitrogen, and quantitative experiments showed that it was formed to the extent of 27 to 30% of the nitroguanidine taken. This corresponds to a molar ratio of nitrogen to nitroguanidine of 1:1. This suggests,[1] although we are unable to offer complete experimental proof at present, that nitroguanidine (a mixed anammonide of aquo nitric acid and an ammonocarbonic acid) is in some way subject to dearrangement[5] during the reaction (since nitroguanidine had been recovered unchanged from its solution in liquid ammonia or from a liquid ammonia solution of sodium amide) to form another ammono carbonic acid, cyanamide, and a mixed aquo ammono nitric acid, such as $NH_2 \cdot NO_2$ (nitro-amide) which may be reduced to a mixed aquo ammono nitrous acid. This latter group is known to be unstable, giving N_2.[6] An examination of nitroamide in liquid ammonia with active metals is contemplated. Attempts to prepare aminoguanidine by reduction of a liquid ammonia solution of nitrosoguanidine with metallic sodium gave the same results as with nitroguanidine; no aminoguanidine was obtained.

It was found, however, that the nature of the reduction was changed profoundly if it was carried out in the presence of a solution of ammonium chloride in liquid ammonia. Here no color changes were observed, the solution of nitroguanidine and ammonium chloride remained colorless and only sodium chloride precipitated. Aminoguanidine was obtained only when the molar ratio of nitroguanidine to ammonium chloride was maintained at 1:6. At concentrations of ammonium chloride below this ratio, brilliantly red to reddish-brown substances, containing only small amounts of aminoguanidine, were obtained. Figure 1 summarizes the chief results obtained. It will be observed that by maintaining the molar ratio of nitroguanidine to ammonium chloride constant at 1:6, the hydrazino-(aminoguanidine) formation, as determined by the procedure of Jamieson,[7] is proportional to the molar quantity of sodium added. Substitution of ammonium acetate for ammonium chloride is without effect on the yield (Curve III, Fig. 1); however, doubling the concentration of ammonium chloride considerably lowers the formation of aminoguanidine (Curve II, Fig. 1). The aminoguanidine was identified by its conversion to benzalaminoguanidine, $C_6H_5CH{=}NNHC(NH)NH_2$; m. p. found, 178.5°; reported 178.[8]

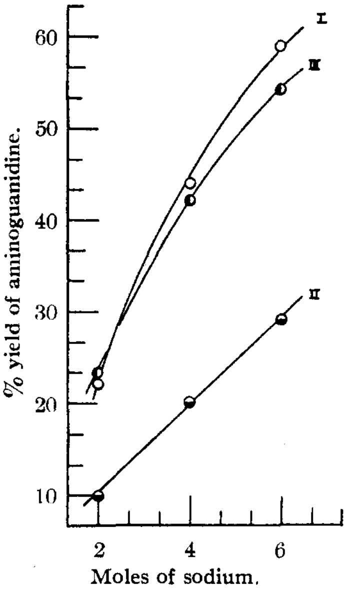

Fig. 1.—I, ○, nitroguanidine : ammonium chloride, 1:6; II, ◒, nitroguanidine : ammonium chloride, 1:12; III, ◐, nitroguanidine : ammonium acetate, 1:6.

Anal., Calcd. for $C_8H_{10}N_4$: N_2H_4, 19.75. Found: N_2H_4, 19.69. The yields of aminoguanidine for the ratio, sodium : nitroguanidine : ammonium chloride, 6 : 1 : 6, varied from 50 to 60%. By adding a mixture of sodium and ammonium chloride in the ratio of 1 : 1 to a solution of

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[3] Audrieth and Schmidt, University of Illinois, private communication, found substantially the same for nitroguanidine and sodium in liquid ammonia.

[4] Several values for the melting point of cyanamide can be found in the literature; 40° appears to be the average value given.

[5] Davis and Abrams, *Proc. Am. Acad. Arts Sci.*, **61**, 437 (1926).

[6] Franklin, "The Nitrogen System of Compounds," Reinhold Publishing Co., N. Y., 1935, p. 288.

[7] Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926, p. 36.

[8] Thiele, *Ann.*, **270**, 35 (1892).

nitroguanidine in liquid ammonia, yields of 60 to 70% were obtained.

While the ammonium salts of strong acids have been used for decomposition of sodium-liquid ammonia reduction products,[2] this work appears to be the first example in which an acidic solution of liquid ammonia was used to change the environmental condition of the liquid ammonia solvent media during reduction. The importance of the environmental conditions of the solvent media for the reduction of nitroguanidine has been demonstrated.[9] The mechanism will become clear when it is remembered that the ammonium ion is an ammoniated hydrogen ion

$$Na^\circ \longrightarrow Na^+ + e^-$$
$$H^+ + e^- \longrightarrow H^\circ$$

if, however, an oxidant be present

$$\text{Oxidant} + H^+ + e^- \longrightarrow \text{Reductant} + H_2O$$

It, therefore, appears probable that liquid ammonia could also serve as a solvent medium for catalytic hydrogenations in which molecular hydrogen is introduced into a liquid ammonia solution of an oxidant in the presence of a catalytically active metal. We are at present engaged in determining the usefulness of liquid ammonia as a solvent medium for catalytic hydrogenations, and in extending the mechanism of the reduction and behavior of nitroguanidine in that solvent.

(9) Lieber and Smith, This Journal, **58**, 2170 (1936).

BROOKLYN, NEW YORK RECEIVED MARCH 26, 1937

Micro Analysis for Exchangeable Hydrogen

BY WILLIAM H. HAMILL

A technique has been developed for the determination of exchangeable hydrogen with 2–5 mg. of substance (water soluble, non-volatile) and 50–100 mg. of heavy water (98%) which is correct within 3%. The determination depends upon the decrease in density of the heavy water, due to exchange, as measured by a small quartz float[1,2] controlled by temperature at constant pressure. The density of the float was determined with potassium chloride solution, part of which was used for a pycnometric density determination at the same temperature as that required for flotation equilibrium.

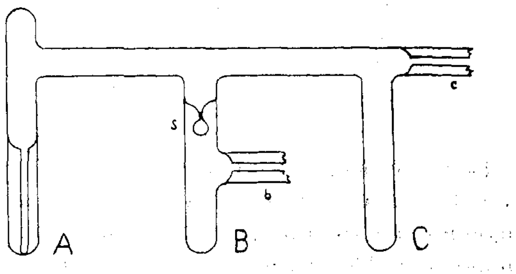

Fig. 1.—Exchange vessel.

Exchange analyses were made in a Pyrex vessel, hereafter referred to as the still (Fig. 1). The float was introduced into the capillary A, the substance into B and the heavy water, in a sealed ampoule, into C. The still was evacuated to about one micron through b and c and sealed. The heavy water was released by immersing C in dry ice, the freezing water shattering the ampoule, and distilled into A for a density measurement. The water was then distilled into the bulb-seal which was broken by freezing in dry ice.[3] The substance was dissolved and the water distilled off quickly at room temperature by cooling C with dry ice. The water was then distilled into A and the density redetermined. This process was repeated to ensure complete solution and exchange.

The number of exchangeable hydrogen atoms per molecule of substance was calculated from equation (1) with a parallel experiment upon a reference substance to minimize errors arising from exchange with glass, temperature coefficient of density of heavy water, etc. Three determinations with urea served for reference.

$$n_1/n_2 = W_1M_1\Delta t_1S_2N_2/W_2M_2\Delta t_2S_1N_1 \qquad (1)$$

n = number of exchangeable hydrogen atoms per molecule
S = weight of substance
M = molecular weight of substance
N = mole fraction D_2O after exchange
W = weight of heavy water
Δt = difference in flotation temperatures due to exchange

The results of these analyses appear in Table I and refer to immediate exchange (three minutes) at room temperature except as noted. Ogawa's[4] observation of slow exchange for urea (60% in five minutes) was not confirmed. Hydrogen in the methylene group of malonic acid has been shown

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(1) The float, about 8 mm. × 0.6 mm., is maintained upright by means of a quartz bead at one end. The float accelerates 0.01 cm. sec./1° at 30–35°. The effect of pressure upon the density of the float, with respect to heavy water, is only $1(10)^{-5}/1$ atm.

(2) A Pyrex micro float has been employed by Goldfinger and Scheepers, *Compt. rend.*, **198**, 1916 (1934).

(3) This seal is easy to make and positive in action, not failing once. The water freezes quickly at the constriction, sealing the bulb which is broken within two minutes.

(4) Ogawa, *Bull. Chem. Soc. Japan*, **11**, 367 (1936).