TABLE I

Constant		Value	Earlier values
Boiling point (760 mm.), °C.		128.9	128–130,[a] 128.3[b]
Freezing point, °C.		-4.9 ± 0.1	
Density, g./cc.		0.9994 20/4° vac.	1.0008 20/4°,[a] 1.0016 20/20°[b]
Refractive index, n^{20}_D		1.4545	1.4540[a]
Molecular refraction	observed	23.60	23.54[a]
	calcd.[c]	23.72	
Viscosity, poises at 20°		0.0223	
Surface tension at 20°, dynes/cm.		37.5	
Parachor	observed	215.7	
	calcd.[d]	213.3	

[a] Knorr, *Ann.*, **301**, 1–10 (1898). [b] Wilson, *Ind. Eng. Chem.*, **27**, 870 (1935). [c] Atomic refractions from Eisenlohr, *Z. physik. Chem.*, **75**, 605 (1911); **79**, 134 (1912). [d] Atomic parachors from Bayliss, THIS JOURNAL, **59**, 444 (1937); Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

Experimental

Commercial morpholine, purchased from Carbide and Carbon Chemicals Corporation, was added gradually to slightly more than a molar equivalent of oxalic acid dissolved in alcohol. The precipitated morpholine hydrogen oxalate was filtered out and recrystallized twice from 60% ethanol. Even then it did not melt sharply, but sintered and decomposed with effervescence at 190–195°. Titration with standard alkali gave indistinct end-points because of the morpholine liberated by hydrolysis; hence the oxalate was titrated with 0.1 *N* potassium permanganate. Molecular weight found: 178, 178; calcd. for $C_4H_8ONH(COOH)_2$, 177. Morpholine hydrogen tartrate was prepared similarly; it melts at 165–166°.

Morpholine was regenerated from the oxalate by adding the salt to concentrated aqueous potassium hydroxide. The layer of free base was separated and dried over solid potassium hydroxide and then sodium. It was then fractionally distilled from sodium through a three-ball Snyder column. After the first quarter had been set aside for further drying, the remainder had a corrected boiling point of 128.9°. This temperature was read on two thermometers, each newly calibrated with pure chlorobenzene and ethylene dibromide to avoid stem correction. Later distillations showed that it is unnecessary to subject good commercial morpholine to the oxalate method of purification; refluxing over sodium followed by fractionation gave a product of boiling point identical with that of the "purified" material.

The freezing point of freshly distilled morpholine was measured with several thermometers calibrated at 0° with pure ice. The refractive index at 20.0° was determined with a Zeiss dipping refractometer in a closed cell. At the same temperature, the surface tension relative to water was measured with Traube's stalagmometer, and the relative viscosity with an Ostwald viscometer. In all cases precautions were taken to exclude moisture and carbon dioxide from samples tested.

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The Heat of Combustion and Structure of Cuprene

BY P. J. FLORY

In a recent study of cuprene formed by alpha ray polymerization of acetylene, Lind and Schiflett[1] have reported 265.3 kcal. for the heat of combustion per structural unit $-(C_2H_2)-$. Although the structure of cuprene has never been determined, they have calculated the heat of polymerization assuming the formation of one C=C and one C—C bond in place of each C≡C bond of acetylene and using Fajans'[2] heats of atomic linkages. The significance of the comparison of this calculated heat of polymerization with that deduced from the heats of combustion of acetylene and of cuprene was obscured by the approximate nature of Fajans' values.

A much more reliable heat of polymerization can be calculated from recent thermochemical data. In conformity with Lind and Schiflett's assumption regarding the constitution of cuprene, a chain structure in which the single and double bonds occur alternately, *i. e.*, $-(CH=CH)_n-$, will be assumed.

Expressing heats of combustion (Q) as heat

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[1] S. C. Lind and C. H. Schiflett, THIS JOURNAL, **59**, 411 (1937).

[2] K. Fajans, *Ber.*, **53**, 643 (1920).

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]

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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).