

NOTE

Catalytic Synthesis of Hexamethylenetetramine.—The catalytic formation of formaldehyde from carbon monoxide, hydrogen and hydrogen chloride¹ and of formamide from liquid ammonia and carbon monoxide² suggested to us the possibility of forming the more stable hexamethylenetetramine catalytically from carbon monoxide, hydrogen and ammonia.

To test this possibility, a mixture of these gases was passed at the rate of about 5 liters per hour into a reaction chamber which contained the catalyst heated to 250–280°. The catalyst—an equal mixture of reduced, finely divided nickel and very pure diatomaceous earth—was evenly distributed throughout a hard glass tube about 60 cm. in length, enclosed in an iron pipe in a combustion furnace.

The gases carried the sublimed hexamethylenetetramine through an air-cooled condenser and by means of an adapter into the bottom of a side-neck distilling flask, which served as a receiver. The exit gases passed through this side-neck into a safety bottle and then into a wash-bottle completely filled with water to dissolve any soluble material. Upon exit the remaining gases were burned.

A small amount of hexamethylenetetramine was formed. This was confirmed by the various chemical reactions and by conversion to the dinitroso-pentamethylenetetramine.³

A relatively large quantity of ammonium carbonate was found in the exit wash-bottle, undoubtedly resulting from the reaction, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$, since a deposition of carbon was noticeable in the reaction chamber. A trace of ammonium cyanide was detected by the test of Liebig.⁴

When the nickel catalyst was replaced by platinized asbestos, no reaction took place. Undoubtedly, the nature of the catalyst in this synthesis must be such that an unstable carbonyl is possible. The carbon monoxide thus liberated, being in a nascent or active condition, may readily combine with the hydrogen present to form formaldehyde which in the presence of the ammonia readily condenses to produce hexamethylenetetramine.

An increased yield of hexamethylenetetramine would presumably be obtained by the use of pressure.

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¹ Church, Fr. pat. 519,649; *Zentr.*, **4**, 653 (1921).

² Meyer and Orthner, *Ber.*, **54B**, 1705–9 (1921). Compare also *C. A.*, **16**, 237 (1922).

³ Griess and Harrow, *Ber.*, **21**, 2737 (1888). F. Mayer, *ibid.*, **21**, 2888 (1888). Compare also Beilstein, "Handbuch der Organischen Chemie."

⁴ Autenrieth, "Detection of Poisons and Strong Drugs," Tr. W. H. Warren, 1909, p. 18.