Studies on Catalytic Action, VII. Catalytic ction of Reduced Copper on Acetaldehyde.

By

Shigeru Komatsu and Masao Kurata.

(Received January 30, 1924).

The polymerisation of acetaldehyde into paraldehyde, as studied by Kekulé and Zincke[1] and also by other chemists[2], was usually accomplished by the aid of heat or the presence of a catalyst. Metaldehyde can only be obtained from acetaldehyde by adding a catalytic agent and cooling to a low temperature, and paraldehyde always accompanied in a greater quantity.

From the behavior of acetaldehyde on heating[3], decomposing into carbon monoxide and methane with a second reaction to some extent yielding ethylene, oxygen, acethylene and benzene, it seems its polymerisation at high temperature will not be attainable.

As a matter of fact, W. Ipatiew[4] has succeeded in getting paraldehyde from acetaldehyde by heating at 360° in presence of alumina, and Sabatier and Gaution[5] have observed that acetaldehyde when heated at 360° in presence of thoria tends to polymerize into crotonic aldehyde and other substances.

1 Lieb. Ann., **162**, 145 (1872).
2 W. R. Orndorff and J. White: Amer. Chem. J. **16**, 50 (1894).
3 M. Berthelot and E. Jungfliesh: Traité elémentaire d. chimie orgn. 1,487 (1908); J. Nef: Lieb. Ann., **318**, 198 (1901); W. A. Bone and H. L. Smith: J. Chem. Soc., **87**, 913 (1905); E. Peytral: Bull. soc. chim., (4), **27**, 34 (1920).
4 Chem. Z., II, 87 (1900)
5 C. R., **166**, 632 (1918).

According to Louguinine's data[1] for the heat of combustion of acetaldehyde, paraldehyde and metaldehyde, the latter substance in the same manner with paraldehyde, can be obtained from acetaldehyde at high temperature.

Accounts of the relation between acetaldehyde, paraldehyde and metaldehyde from the point of view of phase rule, were discussed by H. W. B. Roozeboom[2], by W. D. Bancroft[3], by R. Hollmann[4] and by A. Smits and H. L. de Leeuw[5], and the last named authors especially have settled this termolecular pseudo-ternary system and also confirmed triple point of metaldehyde to be 246.2°.

Consequently, the authors came to believe that there should be a way of getting metaldehyde, if one could find a catalytic agent which should bring a relatively rapid change of acetaldehyde into metaldehyde and a relatively slow change of the latter into paraldehyde.

40 grm. pure acetaldehyde B. p. 22–27° from Merck, were passed on reduced copper heated at 300°, during an interval of $2\frac{1}{2}$ hours, and a clear liquid reaction product with some water and needle crystal was obtained. It amounted to 32 grm. and showed an acid reaction to a litmus paper.

1. Metaldehyde.

The needle crystals separated from the liquid by filtration, were recrystallized from benzene solution and amounted to 0.2 grm.

It was insoluble in water, but readily soluble in hot alcohol, and sublimes without melting and passes into acetaldehyde on heating. It did not act to reduce on ammonical silver solution.

Analytical figures : C=54.55 ; H=9.32 agree with C=54.52 ; H=9.15 for metaldehyde $(C_2H_4O)_3$.

---

1 C. R., **108**, 620 (1889).
2 Z. Phy. Chem., **28**, 659 (1899).
3 J. Phy. Chem., **5**, 182 (1901).
4 Z. Phy. Chem., **43**, 153 (1903).
5 Ibid., **77**, 269 (1911).

On distilling 5 times, the filtrate was divided into the following 4 fractions:

1.	23– 28°	17	grm.
2.	100–122°	0.6	,,
3.	122–130°	3.7	,,
4,	residue	0.3	,,
		21.6	,,

From the residue 0.1 grm. of pure metaldehyde was obtained.

2. Paraldehyde.

The third fraction consisted mainly of the fraction B. p. 123–124°, which was confirmed to be paraldehyde by determination of its physical constants and also by elementary analysis:

$C=50.40$; $H=9.31$; $d_{4^\circ}^{25^\circ}=0.9906$; $n_D^{25^\circ}=1.4016$.

3. Crotonic aldehyde.

A substance which behaves like crotonic aldehyde toward the reducing agents, bromine water and potassium permanganate, was observed to consist of the main portion of the second fraction. An oxime obtained from the fraction by the action of hydroxylamine, which is similar in its properties to crotonic aldehyde.

It was shown experimentally that acetaldehyde on passing on reduced copper heated at 300°, was transformed into paraldehyde and metaldehyde, together with some crotonic aldehyde, and this extraordinary result relating to the formation of metaldehyde from acetaldehyde at high temperature can be accounted for the theory mentioned above.

Oct. 1923, Laboratory of Organic–and Bio–Chemistry.