Experimental Study of the Oxidation of Gaseous Monomethylhydrazine in a Strictly Monophasic Medium

J. Chem. Research (S), 1999, 524–525
J. Chem. Research (M), 1999, 2218–2239

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Intermediate and final products of the oxidation of monomethylhydrazine by dioxygen are studied using an original device which allows analysis of the gaseous medium under strictly monophasic conditions.

The analysis of previous work[1–7] has shown that the oxidation of monomethylhydrazine by dioxygen strongly depends on the experimental conditions. Thus, the first object of this work was the construction of a device aiming at the study of chemical reactions in gaseous medium under stringent monophasic conditions.

An experimental device has been built and is schematically shown in Fig. 1. It allows an accurate definition of the initial medium composition and of initiation of the reaction. In order to attain these requirements, a measured amount of frozen monomethylhydrazine was first vaporized in the vacuum vessel. After introduction of helium, pressurized dioxygen was injected and the extent of the reaction followed by gas chromatography.

In order to avoid any condensation of water[9,10] in the reactor vessel, the monomethylhydrazine oxidation was carried out in helium at 50 °C. The total pressure was adjusted to 1 bar and the initial ratio of the reagents was fixed with $[O_2]/[MMH] = 4$.

The first step of oxidation is fast and complete, and leads to a highly reactive molecule $CH_3-N=NH$. The methyldiazene then reacts with dioxygen present in excess and formaldehyde monomethylhydrazone is formed by different mechanisms as shown in Fig. 2. New final products such as 2,3,4-triazapenta-1,3-diene, 1,2,3,4-tetraazapenta-1,3-diene and 2,3,4,5-tetraza-1,4-diene and intermediate compounds (*e.g.* $CH_3-NH-N=CH_2$) have been characterized by GC MS.

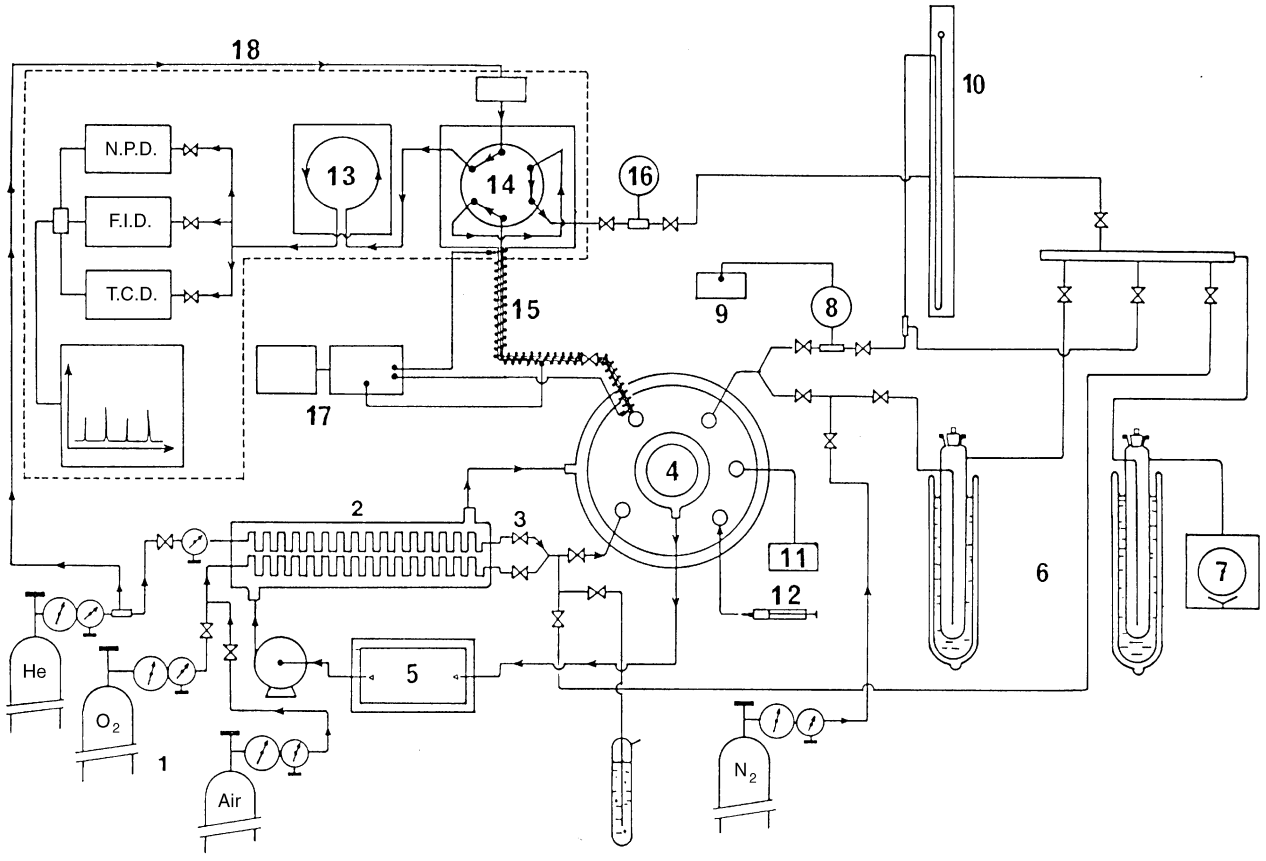

Fig. 1 Experimental device for the oxidation of gaseous monomethylhydrazine in strictly monophasic medium. 1, Gas station : He, O_2, N_2, air; 2, heat exchanger; 3, Millimite gate; 4, reactor vessel; 5, thermostat; 6, liquid air trap; 7, vacuum pump; 8, membrane pressure-gauge; 9, pressure visual indicator; 10, mercurial pressure-gauge; 11, thermocouple; 12, gas syringe; 13, chromatography column; 14, electromagnetic sluice gate; 15, thermostatic stainless steel tube; 16, vacuum gauge; 17, temperature regulator; 18, gas chromatograph HP 6890

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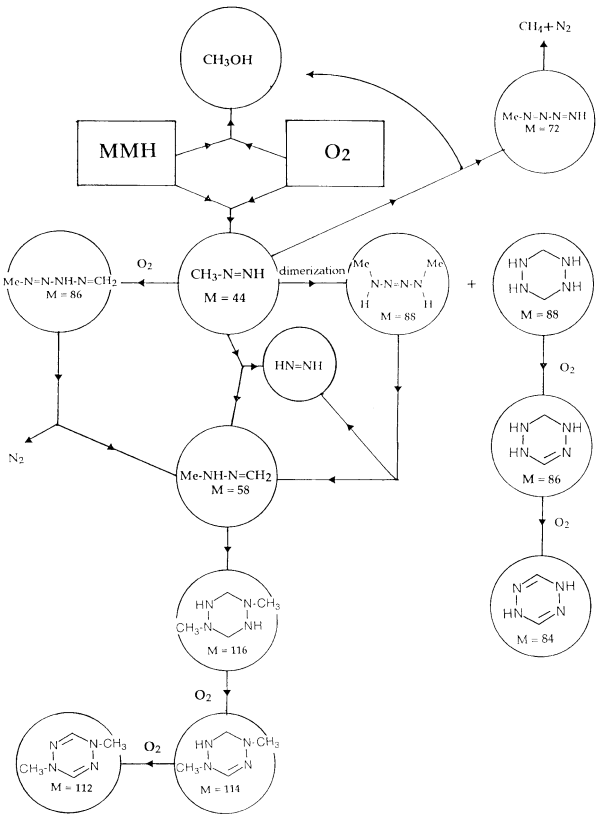

Fig. 2 Reaction scheme of the oxidation of gaseous monomethylhydrazine by dioxygen in strictly monophasic medium

Full text in French

Techniques used: Gas chromatography

Figures: 4

Table: 2

References: 19

Received, 12th April 1999; Accepted, 24th May 1999
Paper F/9/02894C

References cited in this synopsis

1 E. H. Vernot, J. D. McEwen, D. L. Geiger and C. C. Haun, *J. Am. Ind. Hyg.*, 1967, 343.
2 D. A. Stone, Report, ESL-TR-79-10, 1979, 44PP.
3 E. C. Tuarzon, W. P. L. Carter, A. M. Winer and J. N. Pitts, *J. Am. Chem. Soc.*, 1981, **15**, 7.
4 E. J. Bowen and A. W. Birley, *Trans. Faraday Soc.*, 1951, **47**, 580.
5 J. M. Bellerly, Report PERME-Memo-92, BR 74110 1980.
6 G. L. Loper, CEEDO-TR-78-14, paper No. 12, 1978.
7 R. A. Saunders and J. T. Larkins, U.S. NTIS, AD Rep, AD-A027966, 1976, 25PP
9 H. P. Agarwal and B. B. Agarwal, *Ind. J. Chem., Sect. A*, 1979, **17**, 428.
10 J. G. Aston, E. J. Rock and S. Isserow, *J. Am. Chem. Soc.*, 1951, **73**, 1939.