

STABILITY OF HYDRAZINE AS INTERMEDIATE IN PREBIOTIC HYDROTHERMAL CHEMISTRY.

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Introduction: The condition of the emergence and development of life is one of the major scientific questions of all times. It is admitted that the sequence of physico-chemical processes that caused prebiotic chemistry requires catalysis. In the first stages, where redox reaction networks reduced C and N, the mechanisms of reaction in absence of enzymatic catalysis and under geologically plausible conditions is still an open question [1]. Up to now the focus has understandably be on the chemistry of carbon in reduced conditions adequate for the formation of prebiotic organic compounds. Only few studies have addressed the behavior of nitrogen in such reducing environments, in spite of its key role in the natural formation of the elementary bricks of biological macromolecules. In this study we focused on hydrazine (N_2H_4), an intermediate N valence species, as possible reaction intermediate in the natural synthesis of nitrogen bearing organic molecules. Hydrazine is a non-stable molecule acting as an electron donor or acceptor without the need of a catalyst, and may play a role in the physico-chemical processes that caused prebiotic chemistry. It has been identified as trace in experiments using quenched spark discharge through a reduced atmosphere [2] and in the metabolism of contemporary anamox bacteria [3], but there is still a serious lack of thermodynamic data that impedes any simulation of water-rock interaction processes (excepted in the particular fields of industrial applications such as rocket propulsion, car airbags, aqueous circuits of nuclear reactors).

Methodology: In the present study we considered an hydrothermal environment, where the production of H_2 by serpentinisation of ultramafic or komatiite rocks promotes the formation of N_2H_4 . The present project aims at investigating the stability of hydrazine in the ascending fluid. This was achieved through laboratory experiments with in-situ pH-Eh measurements and chemistry monitoring [4] that will allow delimitating various properties: decomposition rate and volatility with temperature, and standard potential of the N_2/N_2H_4 and NH_3/N_2H_4 couples up to 250°C.

Results: Some results are illustrated in Figures 1 and 2. From the experimental data, the stability of hydrazine appears restricted to the acidic range, in particular at high temperature where its thermal decomposition as well its oxidation rate are very fast at high pH. We conclude that given its natural reactivity, hydrazine

may advantageously replace H_2 as electron donor at low temperature.

The identification of the intermediate N-bearing compounds involved in the nitrate and N_2 reduction by H_2 , as well as the detection of hydrazine in the modern environment will also be discussed.

References: [1] Sahai N. *et al.* (2016) *Elements* 12, 398-394; [2] Folsome C.E. *et al.* (1981) *Nature* 294, 64-65; [3] Kartal B. *et al.* (2013) *FEMS Microb. Rev.* 37, 428-461; [4] Million-Picallion L. *et al.* (2015) *J. Solution Chem.* 44, 1900-1919.

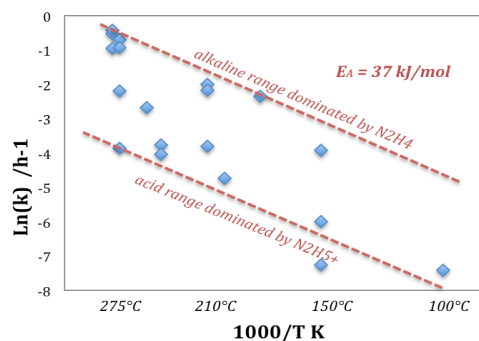


Figure 1: Hydrazine decomposition rate as a function of pH and temperature, for concentrations < 10ppm.

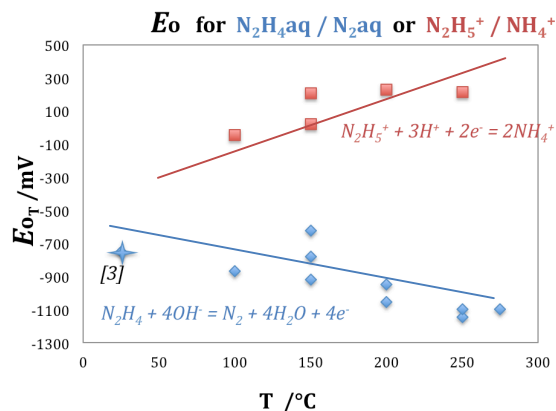


Figure 2: Standard potential for reduction or oxidation of hydrazine, as a function of temperature.