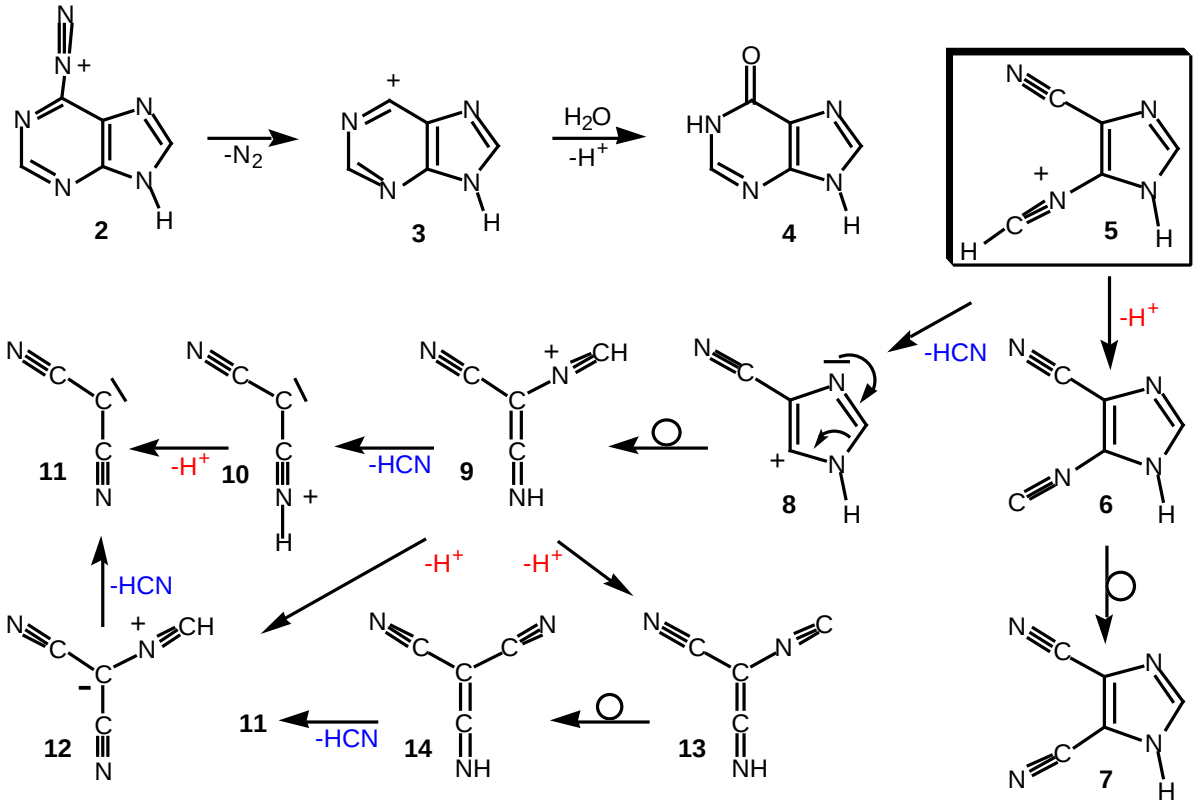
Nitrosative Adenine Deamination. A Quantum Mechanical Study of the Decomposition Pathways of Adeninediazonium Ion.

*Brian Hodgen, Sundeep Rayat and Rainer Glaser**
Department of Chemistry, University of Missouri–Columbia, Columbia, MO 65211

The nitrosative deamination of adenine, **1**, to hypoxanthine, **4**, has been known since the discovery of adenine by Kossel in 1885.[1] This reaction is thought to proceed via the adeninediazonium ion, **2**, and its product of dediazoniation, **3**. In the course of our *ab initio* studies of DNA base deaminations,[2] we have found that **3** is kinetically and thermodynamically unstable with respect to the pyrimidine ring-opened intermediate **5**. This key finding allows one to think about new adenine decomposition pathways.



Two kinds of decomposition pathways are considered. Deprotonation of **5** may lead to **6** or **7** and hydrolysis products thereof are likely side-products of adenine deamination. Three pathways for fragmentation of **5** by loss of two HCN molecules and one proton leading to **11**, were explored to assist the mass-spectroscopic detection of **5** and its derivatives.

¶ Supported by the National Institutes of Health (GM61027)

1 Kossel, A. *Ber.* **1885**, *18*, 79-81.

2 (a) Glaser, R.; Son, M.-S. *J. Am. Chem. Soc.* **1996**, *118*, 10942. (b) Glaser, R.; Rayat, S.; Lewis, M.; Son, M. -S.; Meyer, S. *J. Am. Chem. Soc.* **1999**, *121*, 6108.