

**HYDROTHERMAL REACTIONS OF MODEL AMINES AS PROXIES FOR PREBIOTIC CHEMISTRY.**

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**Introduction:** Exploring the transformation of organic nitrogen compounds under various geochemical conditions is key to better understanding the Earth's modern and ancient global nitrogen cycles, the habitability of other planetary bodies, and the emergence of life [1-6]. Ambient temperature organic nitrogen chemistry is dominantly enthalpy-driven and relatively well understood [7]. However, at higher temperatures reactions become entropy-driven, reaction rates increase, and numerous (often reversible) reaction mechanisms are “unlocked,” resulting in product distributions from experiments and natural systems that conflict with predictions from traditional organic chemistry [8-10].

The past few decades have witnessed an expansion in experimental hydrothermal studies involving nitrogen-bearing organic molecules [e.g., 11-13], mainly amino acids [e.g., 14-16], that provide a foundation for making predictions regarding “biomolecular” degradation, preservation, and synthesis [e.g., 17-19]. The goal of this work is to improve the accuracy and precision of such predictions by using longstanding traditional physical organic chemistry techniques to characterize reaction kinetics, mechanisms, and equilibria.

Model organic compounds were used to investigate hydrothermal organic nitrogen reactions at 250 °C and 40 bar. This work focused on the reaction pathways of benzylamine (C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-NH<sub>2</sub>), which was chosen because 1) its relatively inert aromatic ring allows for the study amine functional group reactivity without significant competing reactions, 2) ring substituents can be used to probe reaction mechanisms [20], and 3) reaction products can be accurately quantified using gas chromatography-flame ionization detection methods [10].

**Mechanistic Kinetics:** pH-buffered time series experiments demonstrate that the kinetics of hydrothermal amine reactivity and resulting product distributions are highly pH-dependent, indicating that the protonated and unprotonated forms of benzylamine undergo different sets of reactions. Contrary to conventional wisdom, many of the hydrothermal products are larger than benzylamine, including dibenzylamine, dibenzylimine, tribenzylamine, and other multi-ring compounds. For both benzylamine and its products, low pH inhibits reduction/oxidation (redox) reactions and promotes ionic reactions, while high pH does the opposite.

At low pH the primary reaction of benzylamine is deamination/hydration to form benzyl alcohol (C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-OH). The mechanism for this reaction was inves-

tigated using benzylamine derivatives with electron withdrawing and donating ring substituents. This investigation revealed two competing deamination mechanisms that were otherwise indistinguishable, as they both produced benzyl alcohol. The two mechanisms have different temperature dependencies, and therefore this finding complicates extrapolation of reaction rates across temperature using Arrhenius methods [21], a reminder for caution when using such methods with reactions whose mechanisms remain unknown.

**Equilibria:** At 250 °C and 40 bar, benzylamine and its products that form via reversible ionic reaction mechanisms reach steady concentration ratios in ca. 3 days, suggesting metastable equilibria is achieved. In contrast, ratios of redox-sensitive species do not stabilize due to certain irreversible reactions, such as the formation of toluene. Collectively, the experimental time series from both equilibria and pH-dependent rate studies were fit with a comprehensive kinetic model that tested the plausibility of various reactions, and ultimately represents a framework toward making accurate predictions regarding organic chemistry in natural systems.

**References:** [1] Berner, R. (2006) *Geol. Soc. Am.*, 34, 413–415. [2] Shock, E. & Canovas, P. (2010) *Geofluids*, 10, 161–192. [3] McCollum, T. & Seewald, J. S. (2007) *Chem. Rev.*, 107, 382-401. [4] Schoonen, A. A. & Xu, Y. (2001) *Astrobiol.*, 1, 133-142. [5] Brandes, J. A. et al. (2008) *Astrobiol.*, 8, 1113-1126. [6] Martin, W. & Russell, M. J. (2007) *Phil. Trans. R. Soc.*, 362, 1887–1925. [7] Clayden, J. et al. (2001) *Oxford University Press* [8] Seewald, J.S. (1994) *Nature*, 370, 285-287 [9] Katritzky et al. (2001) *Chem. Rev.*, 101, 837-892. [10] Yang et al. (2012) *Geochim. Cosmochim. Acta*, 98, 48-65. [11] Abraham, M. A. & Klein, M. T. (1985) *Chem. Prod. Res. Devel.*, 24, 300-306. [12] Katritzky et al. (1990) *Energy & Fuels*, 4, 555-561. [13] Benjamin, K. M. & Savage, P. E. (2004) *J. Supercrit. Fluids*, 31, 301-311. [14] Imai et al. (1999) *Science*, 283, 831-833. [15] Cleaves et al. (2009) *Orig. Life Evol. Biosph.*, 39, 109-126. [16] Fuchida et al. (2014) *Orig. Life Evol. Biosph.*, 44, 13-28. [17] Aubrey et al. (2009) *Orig. Life Evol. Biosph.*, 39, 91-108. [18] Lee et al. (2014) *Chem. Geol.* 386, 184-189. [19] Marshall, W. (1994) *Geochim. Cosmochim. Acta*, 58, 2099-2106. [20] Brown, H. C. & Okamoto, Y. (1958) *JACS*, 80, 4979-4987. [21] Arrhenius, S. (1889) *Zeitschrift für physikalische Chemie*, 4, 226-248.