Abstract: The biochemistry of the nitroxyl system (NO-/HNO), the one-electron reduced congener of nitric oxide (NO), has recently received significant attention, especially as a potential alternative to current treatments of cardiac failure. Compared with NO, however, much less is known about the fundamental solution chemistry of this deceptively complicated system. Due to its inherent reactivity, HNO must be generated in situ, but only a very limited number of appropriate precursors currently exist. Adding to the difficulty of studying HNO chemistry is that a viable method for its direct detection in solution or biologically relevant preparations is not currently available. This presentation will focus on the development of new HNO precursors and new analytical tools for the detection and study of HNO in aqueous solutions, as well as the study of the effects of HNO on proteins involved in calcium cycling.