

INVESTIGATING STRUCTURE AND REACTIVITY RELATIONSHIPS OF NITROGEN-CONTAINING RADICALS WITH COMPUTATIONAL CHEMISTRY AND PHOTOIONIZATION MASS SPECTROMETRY

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Nitrogen-containing organic molecules play significant roles within atmospheric and combustion chemistry due to their presence as volatiles emitted during wildfires, significant components of crude biofuels, and their use in carbon capture technology. The historical focus of gas-phase nitrogen chemistry was on small molecules formed during high-temperature combustion, where the molecular structure of fuel-N has a limited effect on the chemistry due to significant fragmentation. At lower temperatures relevant to Earth's atmosphere and modern combustion technology, oxidation out-competes thermal decomposition and fuel-N structure can have a substantial effect on reactivity. However, the degree to which chemical pathways differ between N-containing compounds is unclear due to the lack of detailed kinetic studies and potential energy surfaces, resulting in poor representation of these pathways within chemical kinetics models. Here, we present the first set of results in a research program designed to build a comprehensive understanding of the structure and reactivity relationships for model nitrogen-containing compounds, with a focus on differences between radical isomers. Five-membered rings pyrrole ($c - C_4H_5N$) and pyrrolidine ($c - C_4H_9N$) serve as model compounds due to their broad chemical importance and ability to form three different radicals. Using KinBot, a computational tool that automatically locates kinetically important stationary points, we have developed potential energy surfaces for reactions of the pyrrolyl and pyrrolidinyl radicals with O_2 at the B3LYP/6-31G level of theory for reaction searches, conformational analyses, and IRC calculations, followed by reoptimization of the most relevant stationary points at ω B97X-D/6-311++G(d,p) with energies refined at CCSD(T)-F12/cc-pVDZ-F12. These results indicate stark differences in reactivity between radical isomers and support our ongoing experimental kinetics studies using a high-pressure laser photolysis reactor coupled to a photoionization mass spectrometer. Characterization of pyrrole and pyrrolidine oxidation will not only provide a detailed knowledge base for future studies of N-containing compounds, but also will allow for comparison to well-studied oxidation pathways of isoelectronic species, such as furan and tetrahydrofuran. Such comparisons will give us a better understanding of the key differences in reactivity between nitrogenated, oxygenated, and pure hydrocarbon volatiles.