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Unveiling the Reaction Mechanism of N-Nitroso Dimethyl Amine Formation from Substituted Hydrazine Derivatives During Ozonation: A Computational Study

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Abstract : N-Nitrosodimethyl amine, the simplest member of the N-Nitrosoamine family, is a carcinogenic and mutagenic agent that has gained considerable research interest owing to its toxic nature. Ozonation of industrially important hydrazines such as unsymmetrical dimethylhydrazine (UDMH) or monomethylhydrazine (MMH) has been associated with NDMA formation and accumulation in the environment. UDMH/MMH - ozonation also leads to several other transformation products such as acetaldehyde dimethyl hydrazone (ADMH), tetramethyl tetra azene (TMT), diazomethane, methyl diazene, etc, which can be either precursors or competitors for NDMA formation.In this work, we explored the formation mechanism of ADMH and TMT from UDMH-ozonation and their further oxidation to NDMA using the second-order Moller Plesset perturbation theory employing the 6-311G(d) basis set. We have also investigated how MMH selectively forms methyl diazene and diazomethane under normal conditions and NDMA in the presence of excess ozone. Our calculations indicate that the reactions proceed via an initial H abstraction from the hydrazine –NH2 group followed by the oxidation of the generated N-radical species. The formation of ADMH from the UDMH-ozone reaction involves an acetaldehyde intermediate, which then reacts with a second UDMH molecule to generate ADMH. The preferable attack of ozone molecule on N=C bond of ADMH generates DMAN intermediate, which subsequently undergoes oxidation to form NDMA. Unlike other transformation products, TMT formation occurs via the dimerization of DMAN. Though there exist a N=N bonds in the TMT, which are preferable attacking sites for ozone, experimental studies show the lower yields of NDMA formation, which corroborates with the high activation barrier required for the process(42kcal/mol).Overall, our calculated results agree well with the experimental observations and rate constants. Computational calculations bring insights into the electronic nature and kinetics of the elementary reactions of this pathway, enabled by computed energies of structures that are not possible to access experimentally.

Keywords : reaction mechanism, ozonation, substituted hydrazine, transition state
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