Title: Unexpected formation of oxygen-free products and nitrous acid from the ozonolysis of the neonicotinoid nitenpyram

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Abstract

The neonicotinoid nitenpyram (NPM) is a multifunctional nitroenamine [$(R_1N)(R_2N)C=CHNO_2$] pesticide. As a nitroalkene, it is structurally similar to other emerging contaminants such as the pharmaceuticals ranitidine and nizatidine. Because ozone is a common atmospheric oxidant, such compounds may be oxidized on contact with air to form new products that have different toxicity compared to the parent compounds. Here we show that oxidation of thin solid films of NPM by gas-phase ozone produces unexpected products, the majority of which do not contain oxygen, despite the highly oxidizing reactant. A further surprising finding is the formation of gas-phase nitrous acid (HONO), a species known to be a major photolytic source of the highly reactive hydroxyl radical in air. The results of application of a kinetic multilayer model show that reaction was not restricted to the surface layers but, at sufficiently high ozone concentrations, occurred throughout the film. The rate constant derived for the O_3–NPM reaction is 1×10^{-18} $cm^3 \cdot s^{-1}$, and the diffusion coefficient of ozone in the thin film is 9×10^{-10} $cm^2 \cdot s^{-1}$. These findings highlight the unique chemistry of multifunctional nitroenamines and demonstrate that known chemical mechanisms for individual moieties in such compounds cannot be extrapolated from simple alkenes. This is critical for guiding assessments of the environmental fates and impacts of pesticides and pharmaceuticals, and for providing guidance in designing better future alternatives.

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